

185-34447

FINAL REPORT

No. 6329-29

on the

DEVELOPMENT OF METALLIZATION PROCESS

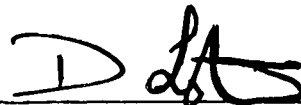
FSA Project, Cell and Module Formation Research Area

Contract 956205

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TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
1.0	INTRODUCTION	1
2.0	CELL MANUFACTURE	2
3.0	THICK FILM PASTES	4
3.1	PASTE EVALUATION	4
3.2	PROCESS REFINEMENT	5
3.3	ADHESION STUDIES	16
3.4	CO PROCESSING	18
3.5	ITO INVESTIGATIONS	20
3.6	NON-LEAD FRIT PASTE	23
3.7	MIXED PASTE	23
4.0	ELECTRINK INKS	37
4.1	INITIAL MATRIX	37
4.2	ADDITIONAL PASTES	55
5.0	TWO-STEP PROCESS	82
6.0	HOT STAGE SEM	86
7.0	CONCLUSIONS AND RECOMMENDATIONS	96

Section 1.0

INTRODUCTION

The object of this contract was the optimization, evaluation, and demonstration of a novel metallization applied by a screen printing process. Based on previous results of JPL contract #955725 "High Resolution, Low Cost Solar Cell Contact Development," a paste consisting of molybdenum, tin, and titanium hydride was selected as the promising composition.

Section 2.0

CELL MANUFACTURE

The process for cell manufacture was fixed at the onset of the program. The traveler used is shown in Figure 2.1. The starting material was 3" round, 15 mil thick, 7-14 ohm-cm, 1-0-0, type P silicon. Silicon was bought from Smiel. Cell preparation began with a 30% NaOH etch followed by phosphine diffusion. Al paste was then screen printed on the back and fired to form the p+ layer. The backs were cleaned and a 2.1" x 2.1" square wafer was laser scribed out of the round wafer. These square wafers are then the basis for subsequent processing.

CELL MANUFACTURING

PRODUCTION LOT NO: _____

START DATE: _____

Silicon

Manf -	Resist -
Type -	PO #
Orient -	Size -
Thickness-	Series # -

OPERATION	DATE	OPERATOR	NO. OF CELLS			REASON FOR REJECTION	
			START	GOOD	BAD		
SURFACE PREPARATION							
DIFFUSE							
PRINT AL BACK							
FIRE AL BACK							
CLEAN BACK							
LASER SCRIBE							
PRINT							Screen - Paste -
PREFIRE							Furnace - Gas -
PREFIRE							Furnace - Gas -
FIRE							Furnace - Gas -
FIRE							Furnace - Gas -
FIRE							Furnace - Gas
FIRE							Furnace - Gas -
TEST							
AR COAT							
TEST							

Figure 2.1

CELL TRAVELER FOR METALLIZATION PROGRAM

Section 3.0

THICK FILM PASTES

Six screen printing pastes were prepared by Thick Film Systems, Inc. at the onset of this contract. The pastes were 80-85% solids and used Thick Film Systems, Inc. vehicle #3347. This vehicle is a cellulosic vehicle used in their silver pastes. The following table shows the solids contents in parts by weight:

TYPE TFS#	Mo	TiH	Sn	Frit
A DP-E570	19.5	80.0	0.5	0
B DP-E571	50.0	49.5	0.5	0
C DP-E572	70.0	29.5	0.5	0
D DP-E573	49.0	49.0	2.0	0
E DP-E574	48.0	48.0	4.0	0
F DP-F503	19.5	80.0	0.5	5.0

Mo refers to Sylvania 280-350 molybdenum powder, Sn refers to Atlantic Equipment Engineers SN 266 tin powder, TiH refers to Ferro Plant Px-41 titanium hydride powder, and frit refers to a proprietary Thick Film Systems Inc. lead-borosilicate frit.

3.1 PASTE EVALUATION

Type A paste was used exclusively for the initial evaluations. Procurement problems initially forced the use of a round front metallization pattern on a square wafer. This pattern led to high series resistance. Screen printed silver cells were used as con-

trols. The IV curve for the best silver cell is shown in Figure 3.1.

This cell has no AR coating. The shunt resistance was measured at 0.5V reverse bias and found to be 25.0 ohms.

The first parameters used for evaluation were a prefire in an IR belt furnace followed by firing in a 5% H₂/95% N₂ atmosphere. Cells were prefired at 500°C at various belt speeds. The cells were then fired for 30 minutes in the reducing atmosphere at 400-600°C. The cells showed poor IV curve caused by shunting and high series resistance. A second experiment tried 450° and 500° prefires followed by shorter firing times at 650°C. These cells were also poor. Next, firing was tried in a 100% H₂ atmosphere. Cells showed metallic-like contacts similar to silver contacts. Curve shape improved.

The next experiment followed the matrix shown in Table 3.1.

The best cells are those fired at 575° for 1 minute. Prefiring at 18"/minute seems slightly better than 9"/minute. Figures 3.2 and 3.3 are IV curves of the best two cells. Table 3.2 shows the characteristics of these cells compared to the silver controls. The cells have not been AR coated and the AR efficiencies are based on a 32% gain.

3.2 PROCESS REFINEMENT

Eight cells of paste types A-E as well as silver controls were manufactured. The cells of each type were divided into four groups (of 2 each). The four groups were processed as follows:

Figure 3.1
SILVER CELL
NO AR
INEFFICIENT FRONT PATTERN

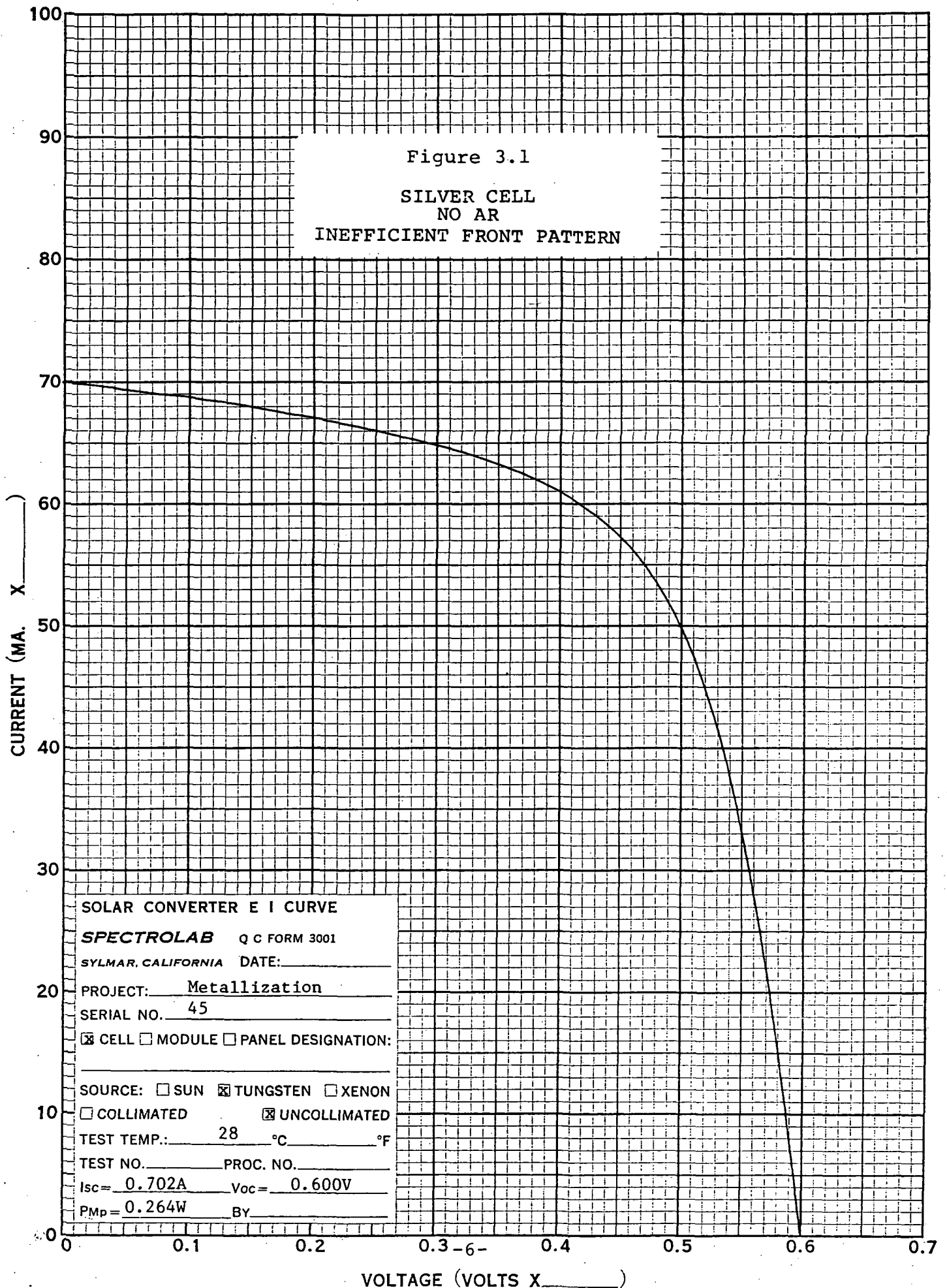


Table 3.1

Prefire	18"/min. 500°	9"/min. 500°	
Fire	30 secs.	30 secs.	
	1 min.	1 min.	} 600°
	2 min.	2 min.	
	5 min.	5 min.	
	1 min.	1 min.	575°
	1 min.	1 min.	550°
	1 min.	1 min.	525°

Figure 3.2
MOLY/TIN CELL
NO AR
INEFFICIENT FRONT PATTERN

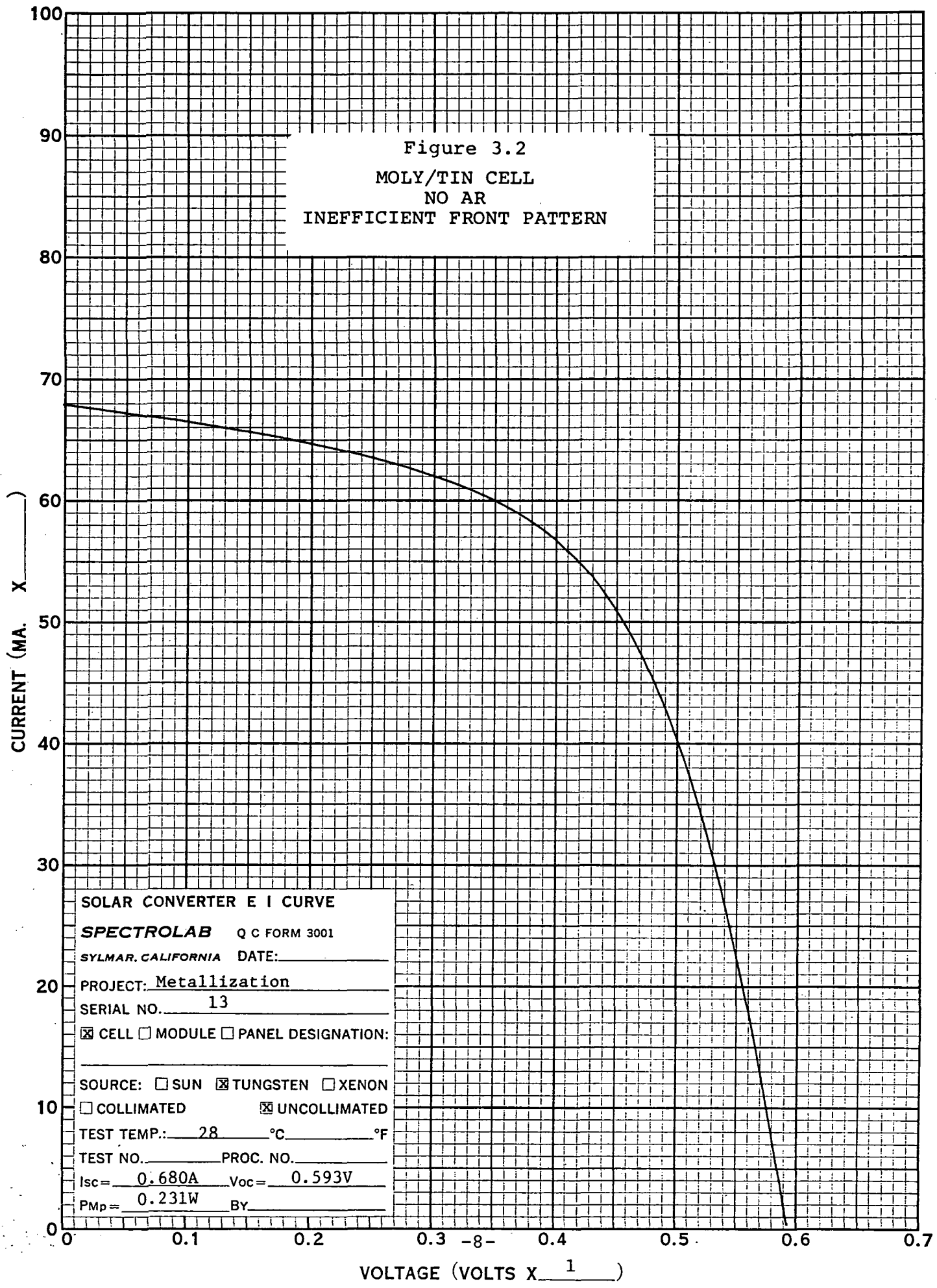


Figure 3.3
MOLY TIN CELL
NO AR
INEFFICIENT FRONT PATTERN

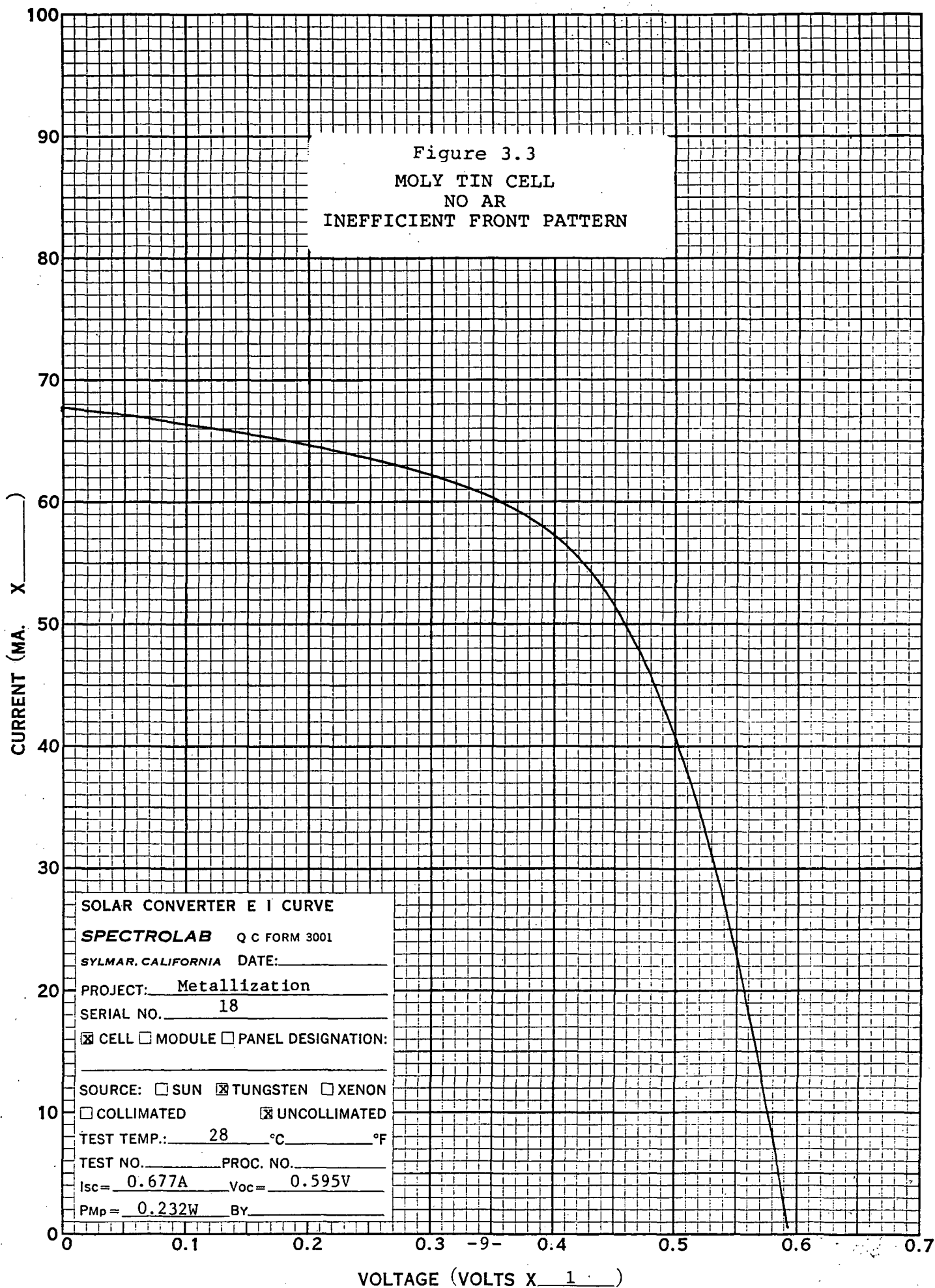


Table 3.2
SUMMARY OF CELL CHARACTERISTICS

Cell #	<u>I_{sc}</u>	<u>V_{oc}</u>	<u>I₅₀₀</u>	<u>I_{mp}</u>	<u>V_{mp}</u>	<u>P</u>	<u>FF</u>	<u>E</u>	(If AR)	<u>R_{shunt}</u>
13 (Mo/Sn)	680	593	409	541	427	.231	.573	8.12	(10.7)	39.7
18 (Mo/Sn)	677	595	411	543	428	.232	.576	8.15	(10.8)	61.7
45 (Ag)	702	600	501	579	463	.264	.627	9.28	(12.3)	25.0

- 1) 18"/1 min. 500°C prefire, 1 min. 575°C H₂ fire
- 2) 18"/min. 500°C prefire, 1 min. 600°C H₂ fire
- 3) 9" min. 500°C prefire, 1 min. 575°C H₂ fire
- 4) 9"/min. 500°C prefire, 1 min. 600°C H₂ fire

The results of this matrix are shown in Table 3.3. The best silver control had $V_{OC} = 601$, $I_{SC} = 700$, $I_{500} = 500$, and $I_{450} = 596$. These cells have no AR coating. The best silver solar cell has an efficiency of 9.3% and a fill factor of 0.627. The best Mo/Sn, Cell #1 from Group A, has a fill factor of 0.609 and an efficiency of 9.0%. If the cells were AR coated, efficiency would rise to approximately 12.3% and 11.9%, respectively. From these results it was decided to continue work using only TFS Type A paste.

A lot of cells was processed using new screens. The front pattern metallization is shown in Figure 3.4. Cells were prefired at 500-550°C at a belt speed of 18" minutes. They were then fired at 575°-625° for 39-90 seconds. Silver controls were processed at the same time.

Figures 3.5 and 3.6 show the best Mo/Sn and Ag cells. The Mo/Sn cell was made using paste Type A with a 200 mesh 1 mil emulsion screen. The Ag cell was made with the same screen. The Mo/Sn cell was prefired at 500°C in an 18" zone at 18"/min. belt speed. It was then fired in H₂ for 90 seconds at 600°C.

The Mo/Sn metallization has a blue-green color after the prefire which becomes metallic after the reduction firing, the appearance

Table 3.3

Paste Type	Pre-Fire Speed @ 500°	Fire Temp. @ 1 min.	Cell #	V _{oc}	I _{sc}	I ₅₀₀	I ₄₅₀
A	9"	575	1	600	701	482	569
A	9"	575	2	598	677	390	490
A	9"	600	3	601	700	469	553
A	9"	600	4	597	696	458	548
A	18"	575	5	603	702	450	543
A	18"	575	7	599	560	286	359
A	18"	600	6	598	701	440	530
A	18"	600	8	602	703	461	550
B	9	575	9	600	687	377	488
B	9	575	11	598	676	297	398
B	9	600	10	600	689	369	478
B	9	600	12	597	644	282	371
B	18	575	13	602	681	345	451
B	18	575	14	602	681	331	438
B	18	600*	15	598	686	409	515
B	18	600*	16	596	692	389	497
C	9	575	20	594	617	194	266
C	9	575	17	589	369	109	150
C	9	600	19	592	668	246	345
C	9	600	18	587	300	90	123
C	18	575	21	597	684	305	415
C	18	575	23	598	667	285	388
C	18	600	22	600	687	350	463
C	18	600	24	596	680	347	458
D	9	575	26	598	684	330	447
D	9	575	25	599	681	320	429
D	9	600	28	598	676	328	435
D	9	600	27	599	678	351	455
D	18	575	31	596	686	346	464
D	18	575	29	598	682	336	448
D	18	600	32	601	691	378	441
D	18	600	30	600	694	393	502
E	9	575	33	596	668	260	356
E	9	575	34	596	639	229	312
E	9	600	35	596	674	265	363
E	9	600	36	598	677	262	417
E	18	575	37	597	672	295	396
E	18	575	38	598	669	286	385
E	18	600	39	597	690	333	440
E	18	600	40	600	685	318	420

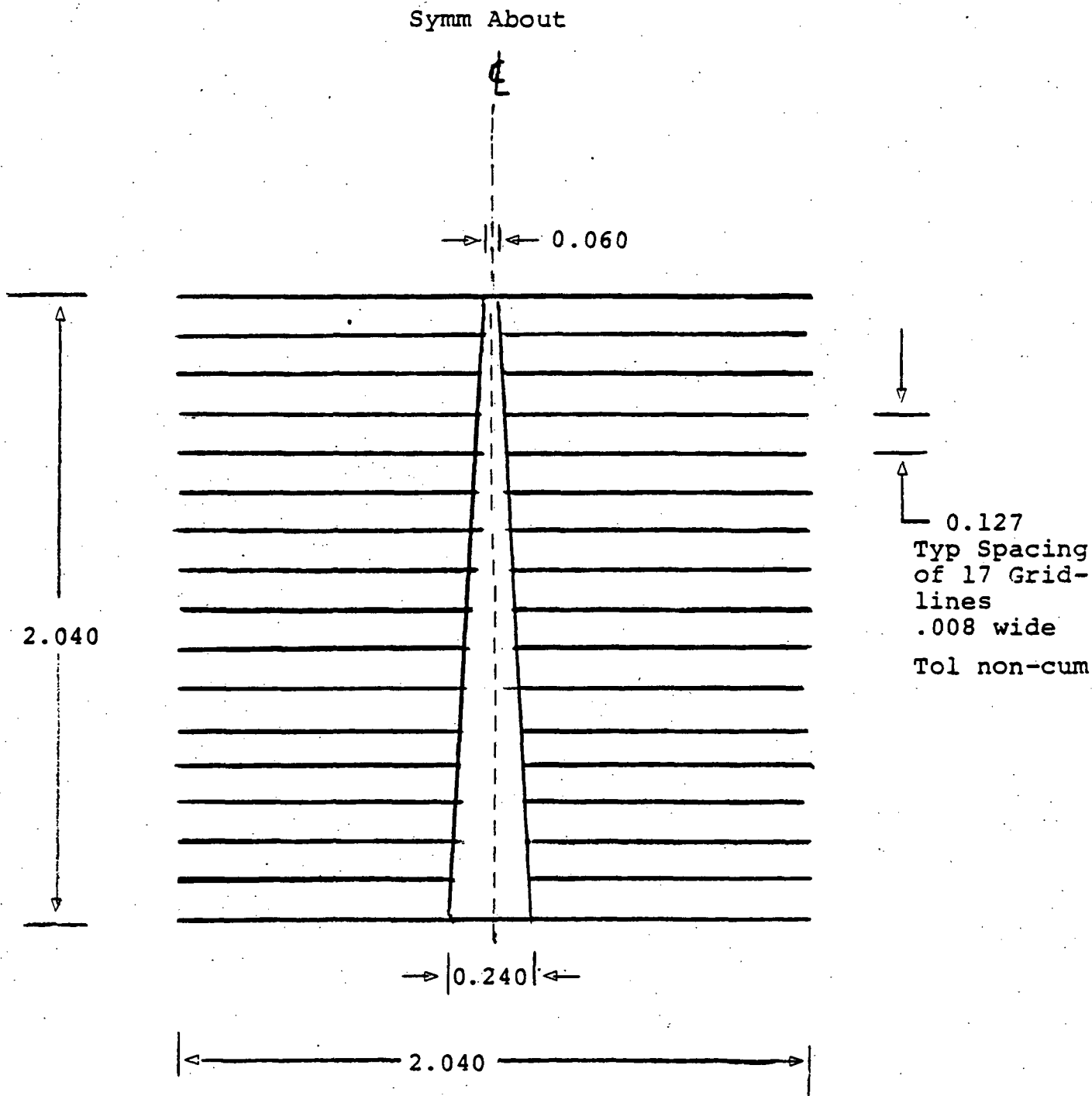


Figure 3.4

FRONT METALLIZATION PATTERN

Figure 3.5

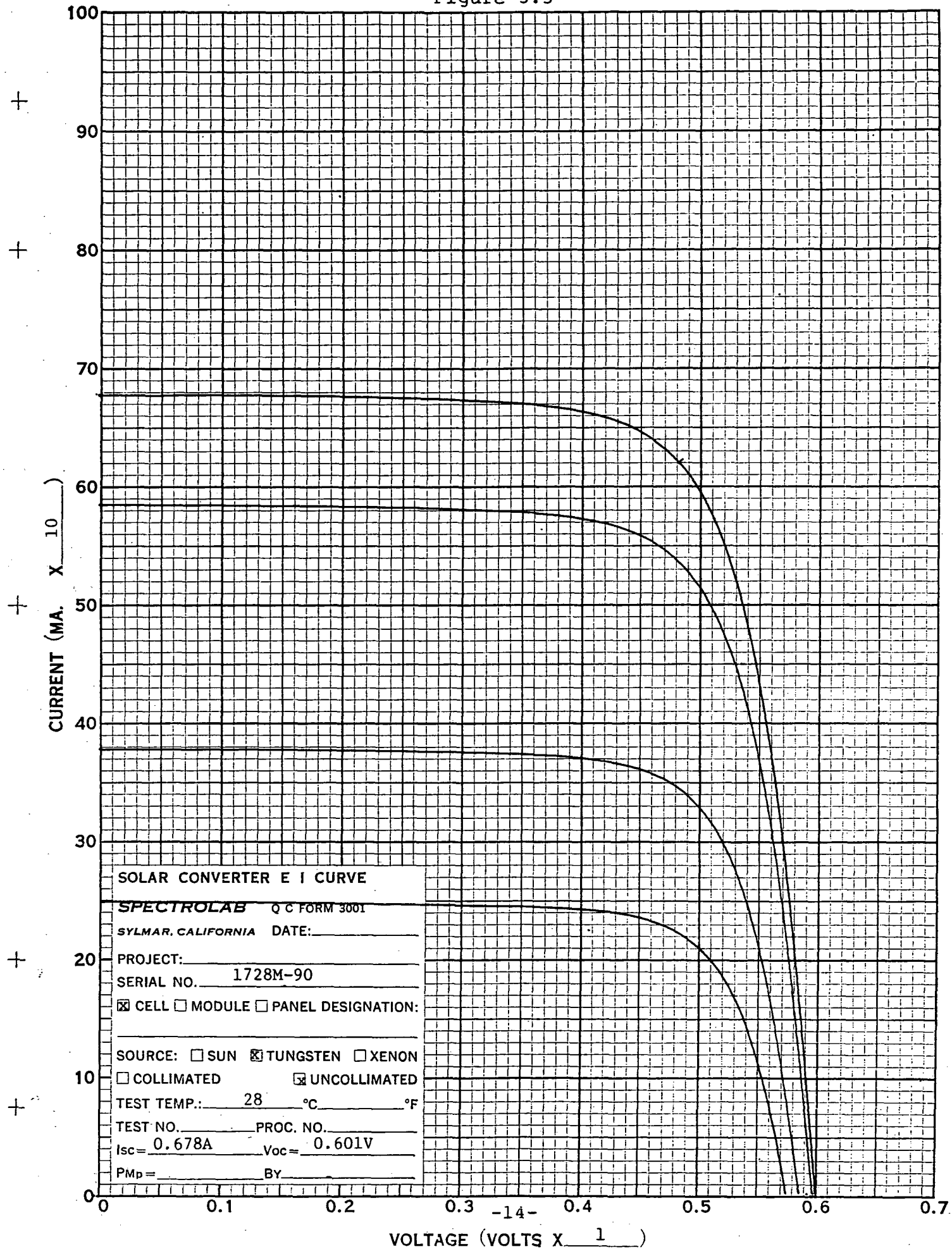
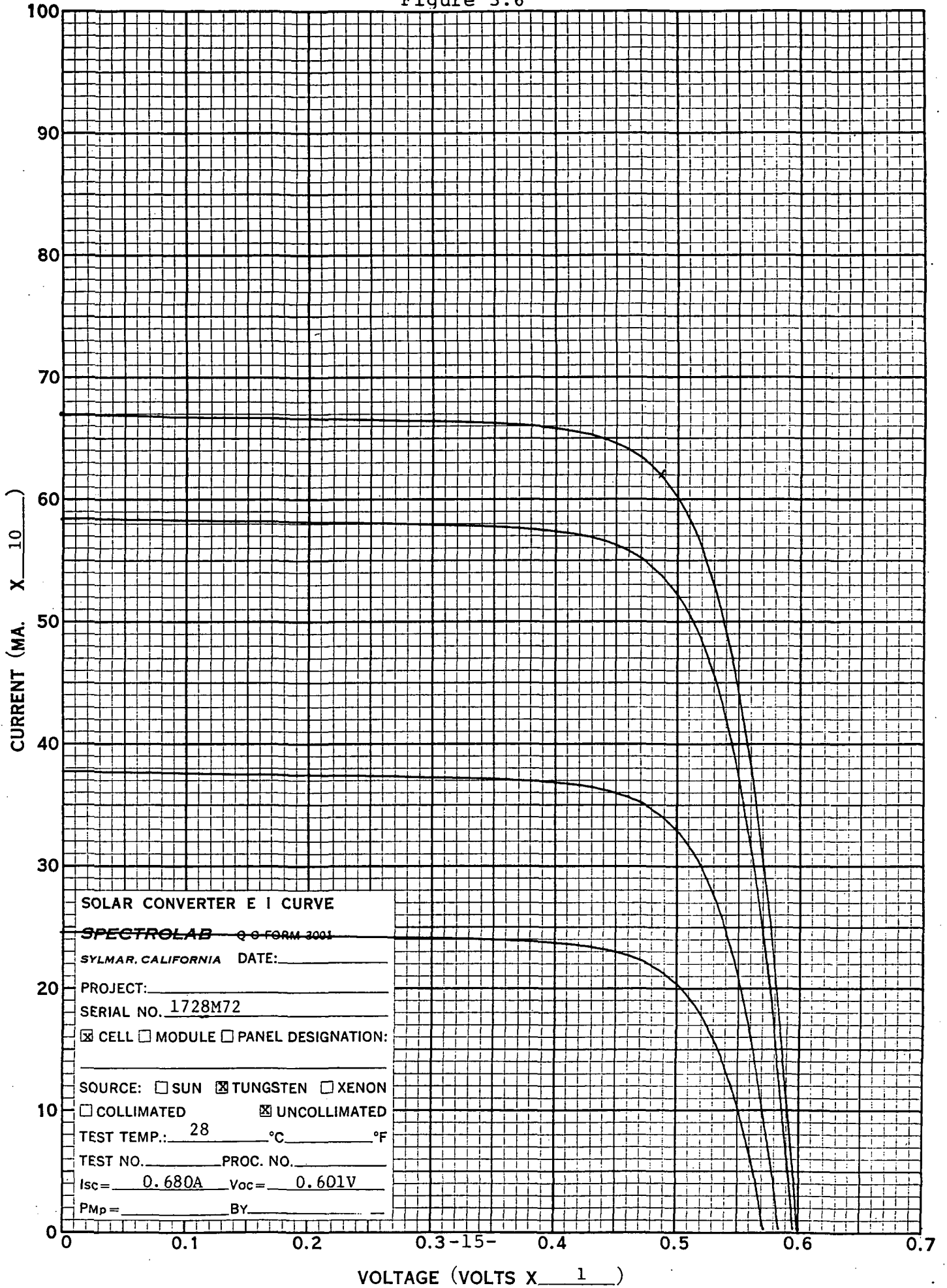


Figure 3.6



is similar to screenprinted silver. If the prefire is at a lower temperature, the initial color is brown and cells shows more series resistance.

The two cells shown in Figures 3.5 and 3.6 have the following characteristics:

<u>Cell</u>	<u>V_{oc}</u>	<u>I_{sc}</u>	<u>I₅₀₀</u>	<u>P_{max}</u>	<u>FF</u>	<u>E</u>
1728M-90 (Mo/Sn)	.601	.678	.596	.229	.73	10.5%
1728M-72 (Ag)	.601	.680	.600	.302	.74	10.6%

Neither cell has an AR coating.

3.3 ADHESION STUDIES

Attempt to solder interconnects to the cell described in Section 3.2 were uniformly unsuccessful. Cells were then manufactured using the F type paste. The F paste showed better adhesion but was still not solderable. Inclusion of the frit did not decrease shunt resistance.

A series of experiments was undertaken to determine if the method of cleaning prior to screenprinting had any effect on adhesion. Table 3.4 shows the variety of cleaning procedures that were tried. Procedure A is our baseline procedure which is used on silver printed cells. All cells showed poor adhesion of the Mo/Sn metallization regardless of the cleaning procedure. The D procedure worked well with silver paste controls and will be used as the standard procedure.

Table 3.4

CLEANING PROCEDURES

A	B	C	D
10% HCl	1 min.	10% HCl	1 min.
H ₂ O	Rinse	H ₂ O	Rinse
10% HF	1 min.	10% HF	1 min.
H ₂ O	Rinse	H ₂ O	Rinse
50% AcOH	1 min.	H ₂ O/NH ₃ /H ₂ O ₂	30 sec.
Hot H ₂ O	Rinse	H ₂ O	Rinse
Acetone	2 min.		
MeOH	2 min.		
Hot H ₂ O	2 min.		
H ₂ O, N ₂	5 min.		

Twenty-five cells were produced using the type F paste containing the lead borosilicate frit. All cells produced were electrically equivalent to silver controls. These cells were fired in air at 18"/min. and 600°C. then reduced for 90 sec. at 650°C. This sequence produced cells which passed a tape pull test 50% of the time.

The cells that passed tape pull were used for soldering experiments. Interconnects were soldered to cells using conventional techniques with tip temperatures varying from 550 to 750°C. No bondings were successful. Interconnects were then soldered using a heated substrate; these attempts were also unsuccessful. Finally, ultrasonic soldering was attempted but was also unsuccessful.

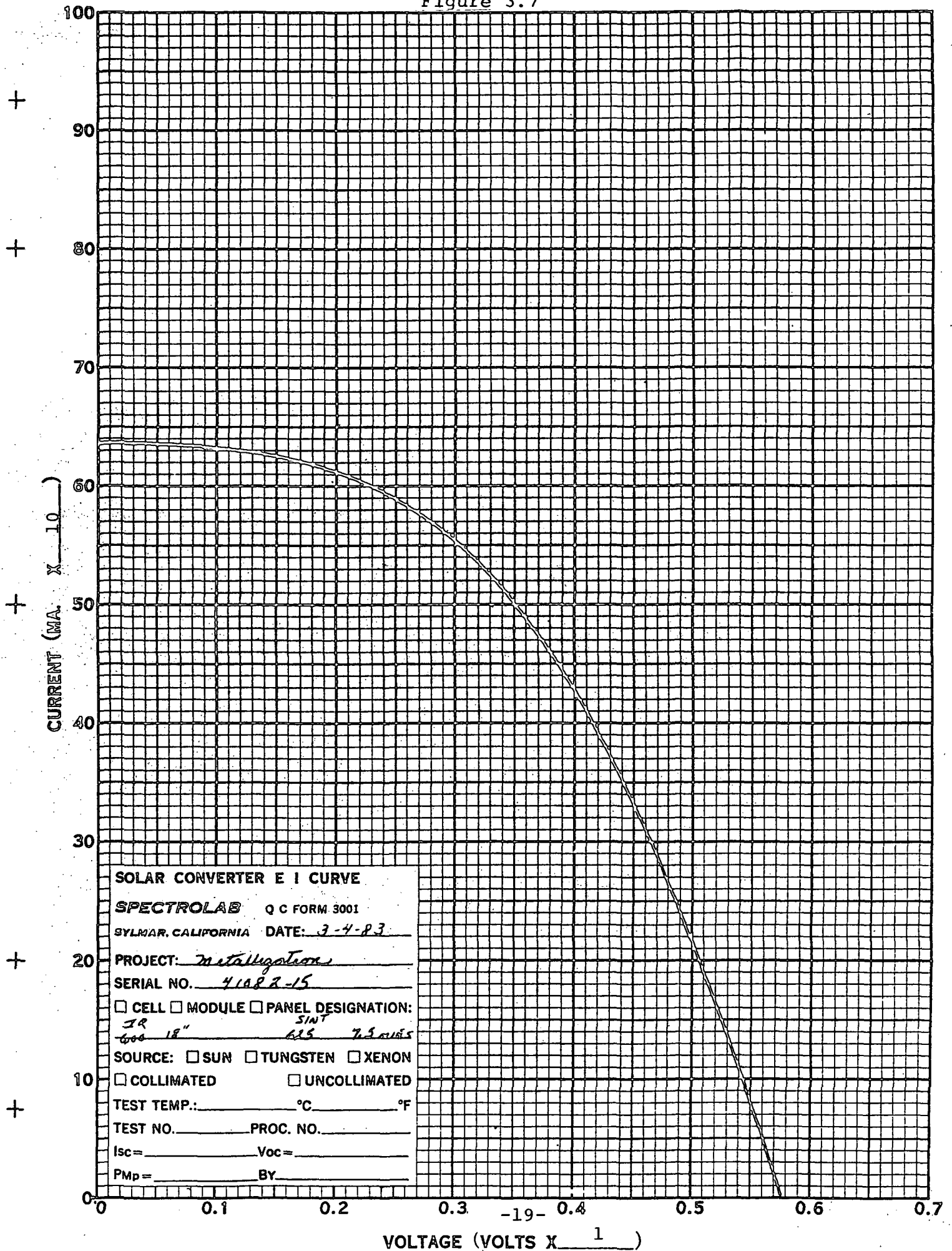
It was concluded that these pastes reduced in hydrogen would not work. It has been theorized that the hydrogen in some way interferes with the bonding to the Si surface. The next section describes using carbon monoxide to replace hydrogen as the reducing agent.

3.4 CO PROCESSING

Carbon monoxide was plumbed into the reducing furnace, allowing the use of either hydrogen or carbon monoxide. Several experiments were run using the CO.

Carbon monoxide reductions were done after oxidative firings at both 550 and 600°C. There was little difference between the results. The cells were then fired at 550, 600, 625, 650, and 700°C. All cells showed high series resistance and poor curve shape. Figure 3.7 shows a typical cell air-fired at 600°C 18"/min.

Figure 3.7



This sequence produced cells which passed a tape pull test 50% of the time but cell characteristics were not acceptable. There was no appreciable lowering of the shunt resistance even when temperatures of 700°C were reached. Figure 3.8 shows a cell reduced at 700°C for 10 min.; little shunting has occurred. Reducing for longer times at lower temperatures increased the series resistance as is seen in Figure 3.9. Cells fired at the longer times (15 min.) also had small tin globules form on the surface.

A group of cells were reduced sequentially in CO and hydrogen and visa versa. These cells showed excellent electrical characteristics similar to H₂ reduced cells but were still unsolderable.

In another experiment a paste was made by adding 3% #3347 silver paste (Thick Film Systems) to the type F paste. This paste was then used with both CO and H reductions. These cells were also unsolderable.

All cells made with the type F paste (Pb/borosilicate frit) passed tape pull tests. Cells made with the type A paste failed. Soldering was always unsuccessful.

3.5 ITO INVESTIGATIONS

Wafers were coated with indium tin oxide (ITO) prior to metallization. The ITO was applied using reactive sputtering by Applied Film Labs Inc. The thickness varied from 512 to 783 Å with an index of refraction of 1.95. The reflected color varied with increasing thickness as follows: green bronze, bronze, purple, blue. The cells were reduced using hydrogen at 600°C. The hydrogen firing also reduced the ITO causing a milky appearance on the

Figure 3.8

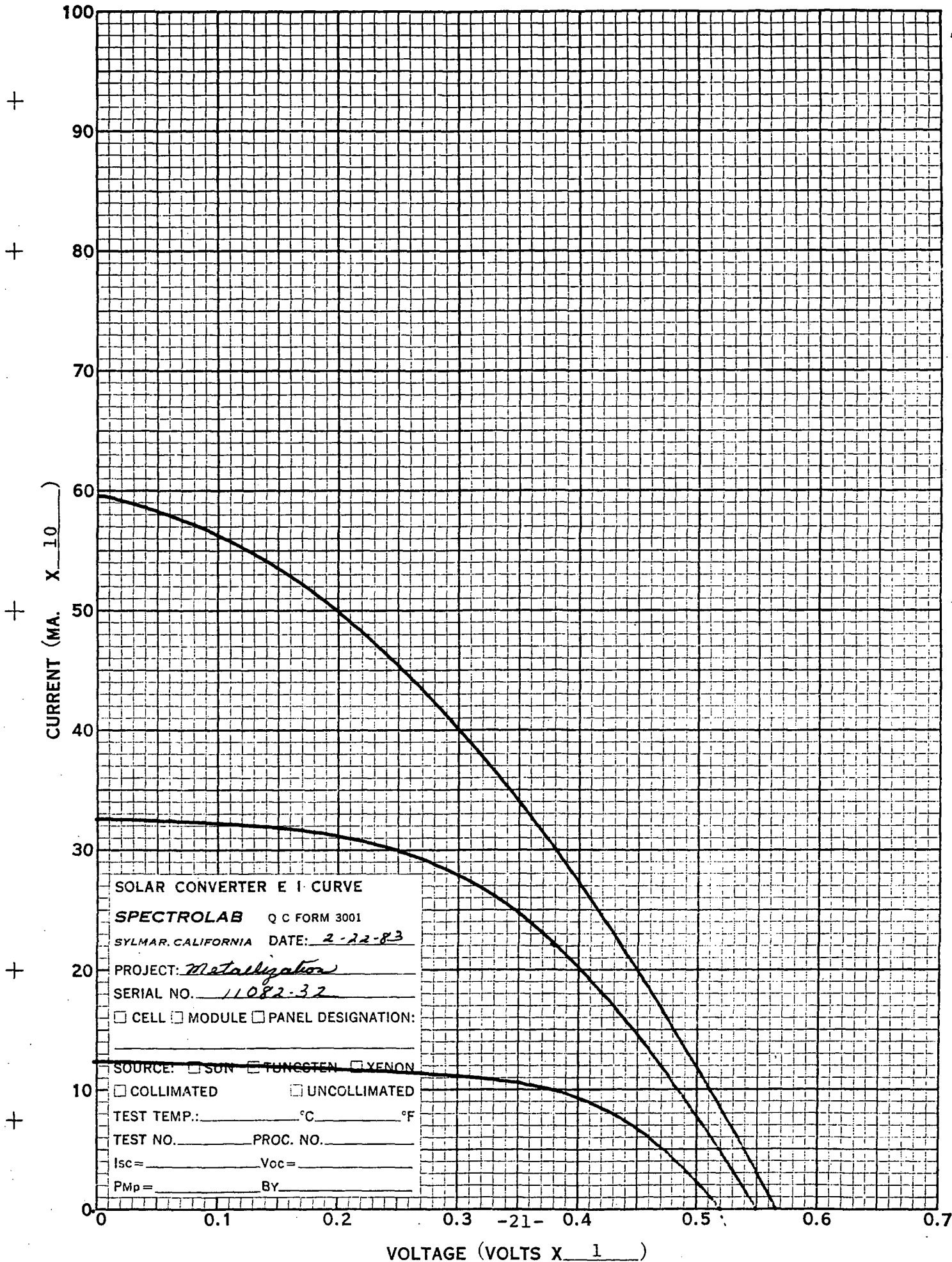
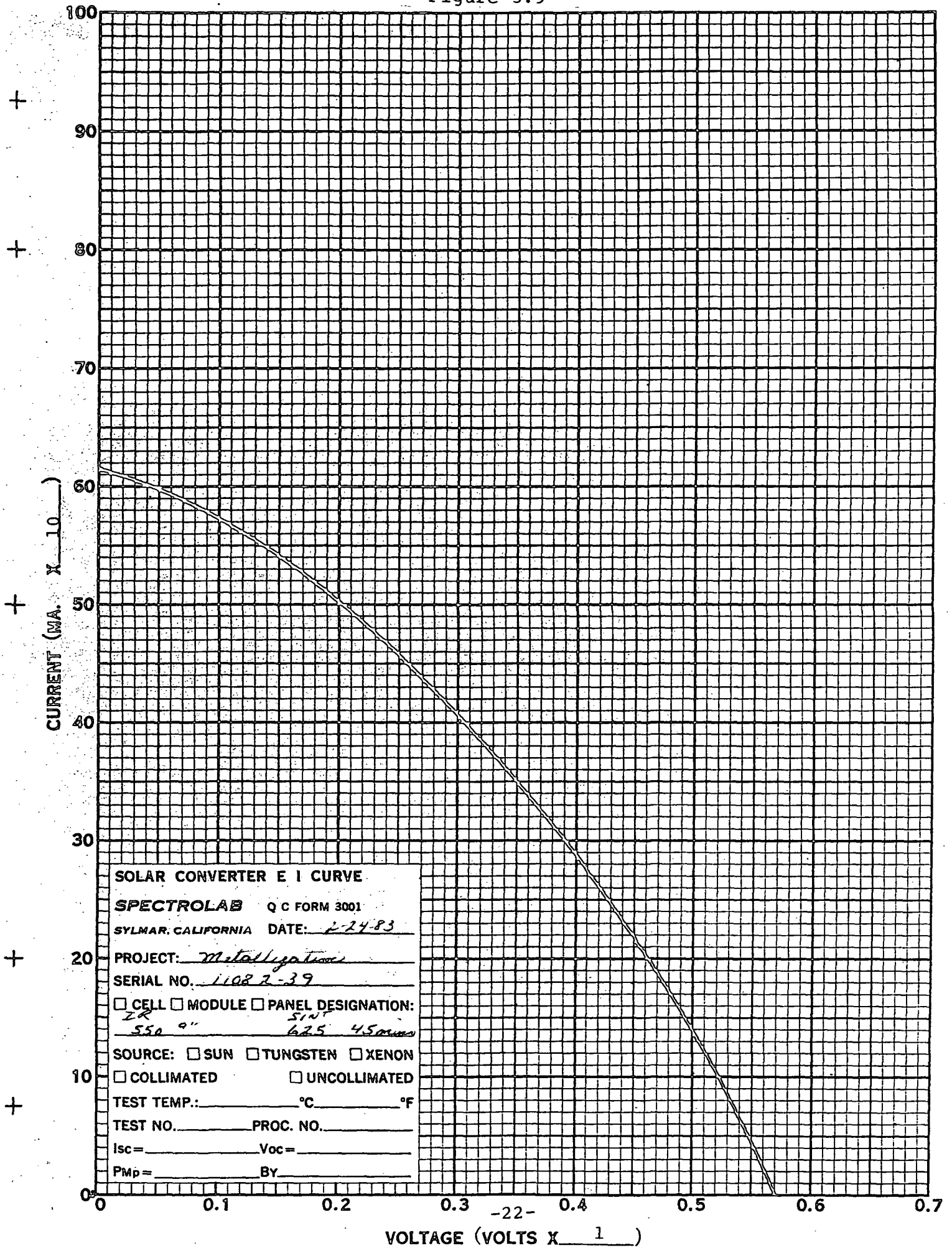


Figure 3.9



cells. Air firing of the cell brought back some of the color of the film and improved cell performance as is shown in Figure 3.10. Attempts to fire the cells at 650°C led to severe shunting (Figure 3.11. Cells were still unsolderable.

Several cells were made by screen printing silver paste over the ITO. Figure 3.12 shows these cells as compared with a conventionally AR coated silver cell. ITO does not appear to be as effective an AR coating as the conventional SiO. This may be due to incorrect thickness, lower index of refraction, or absorption in the ITO.

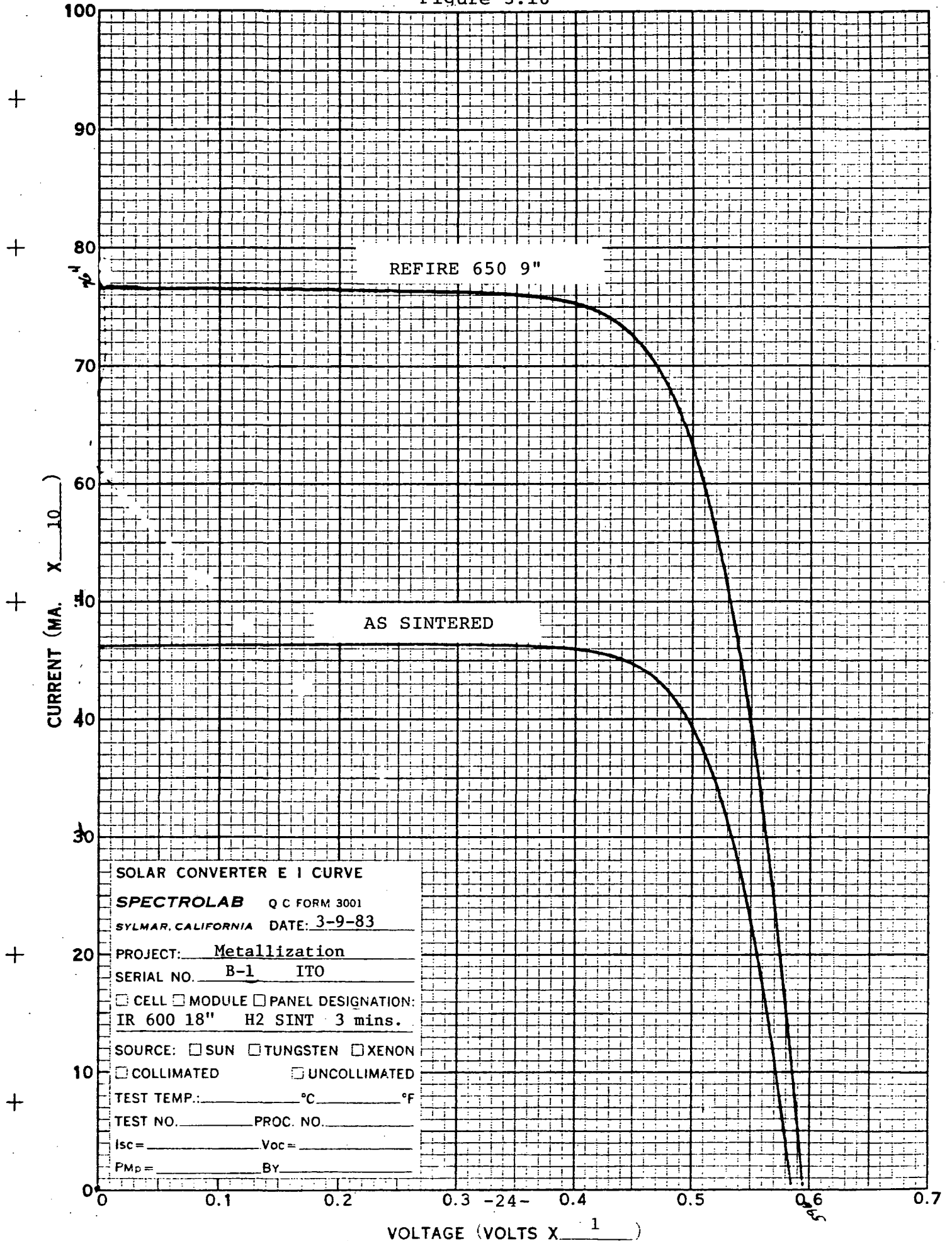
3.6 NON-LEAD FRIT PASTE

A non-lead frit paste was ordered from Thick Film Associates #DP-F523. The paste was the same as the Type F paste except the new frit was substituted for the old type. Table 3.5 shows the characteristics of cells made with this paste. Figures 3.13-3.16 show cells 83, 79, 81, and 85 respectively. As the time of sintering lengthened from 1.5, 5, 10, to 15 minutes at 600°C, the cells first improve as the series resistance decreases, then degrade as shunting occurs. Lower sintering temperatures led to very high series resistance and poor electrical characteristics (Figure 3.17). Soldering was unsuccessful on these cells.

3.7 MIXED PASTE

Another set of experiments was done using paste type F503 to which was added 3% AG3347 silver paste. The cell was first printed with the Mo/Sn, prefired at 600°C, and fired in H at 500°C for 5 min. The silver paste was printed and fired as before. The cell was tested and it was found to have an $I_{500} = .250$; however, there was

Figure 3.10



ITO SHUNTED CELL

Figure 3.11

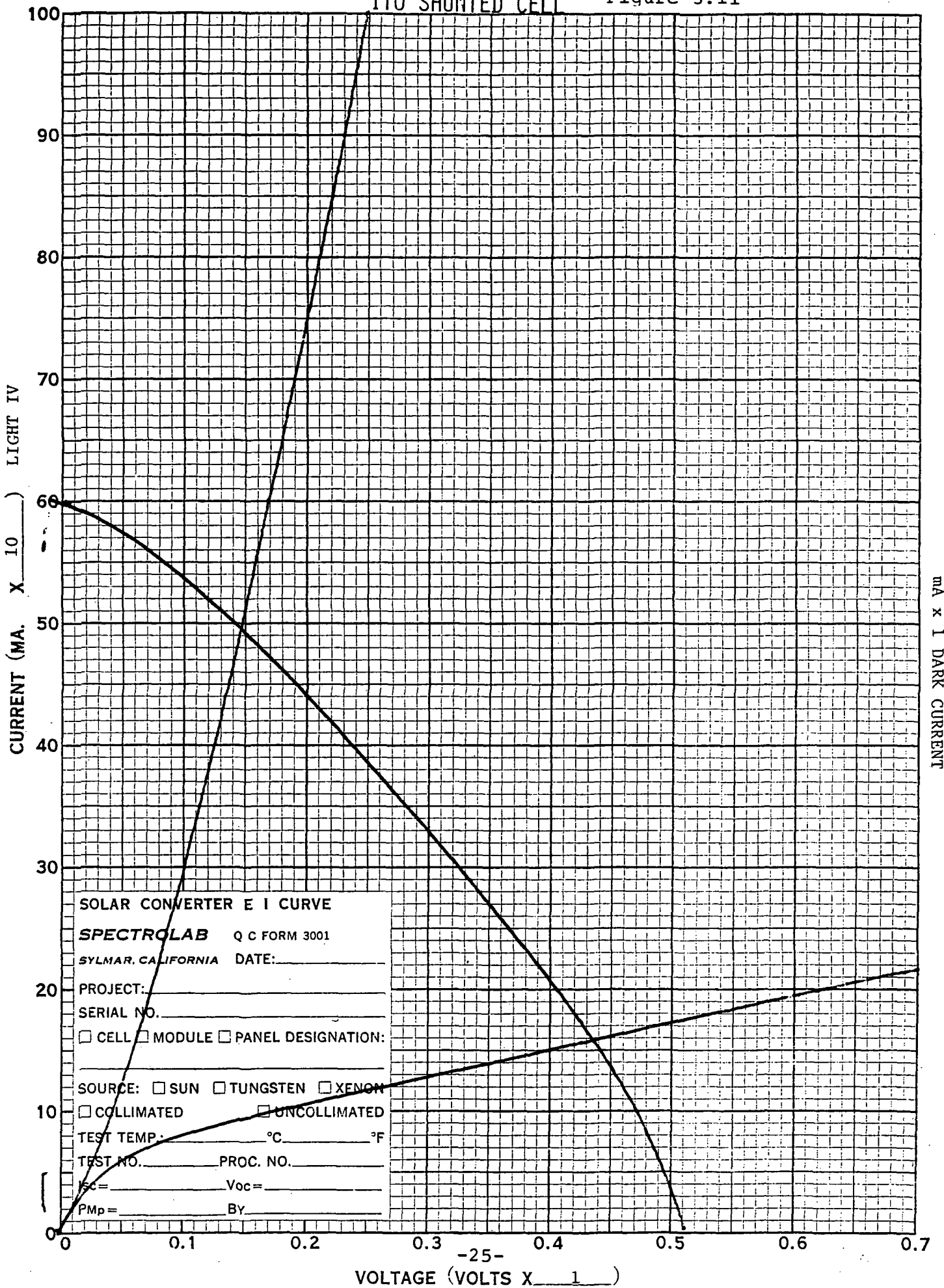


Table 3.5

<u>Cell</u>	<u>Prefire</u>		<u>Gas</u>	<u>Fire</u>		<u>V_{oc}</u>	<u>I_{sc}</u>	<u>I₅₀₀</u>
	<u>Temp.</u>	<u>Belt</u>		<u>Temp.</u>	<u>Time</u>			
41082-70	600	18	H ₂	600	1.5	593	643	351
41082-79	600	18	H ₂	600	5.0	595	646	416
41082-81	600	18	H ₂	600	10.0	591	665	360
41082-85	600	18	H ₂	600	15.0	592	667	353
41082-83	600	18	H ₂	550	15.0	580	654	291

Figure 3.12

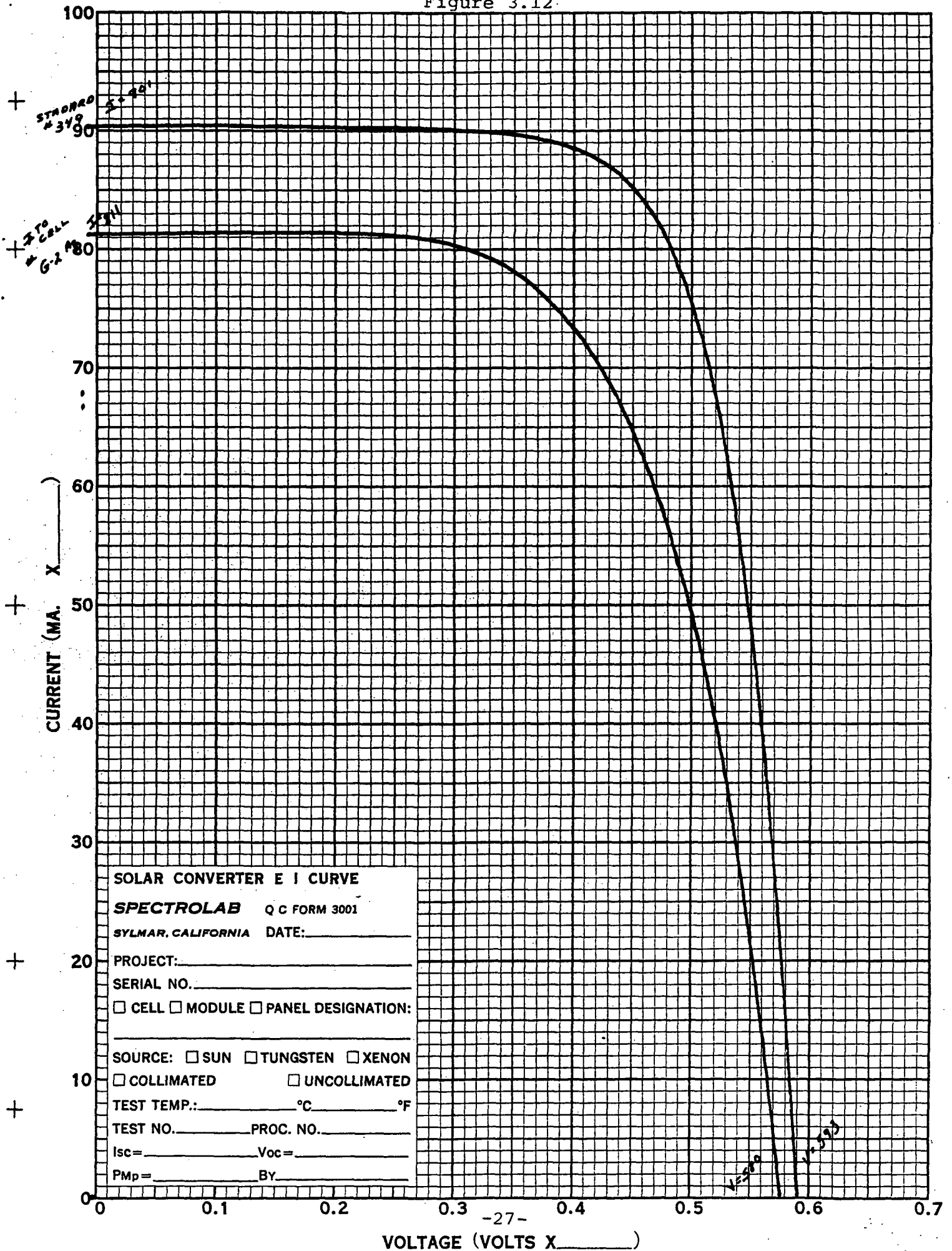


Figure 3.13

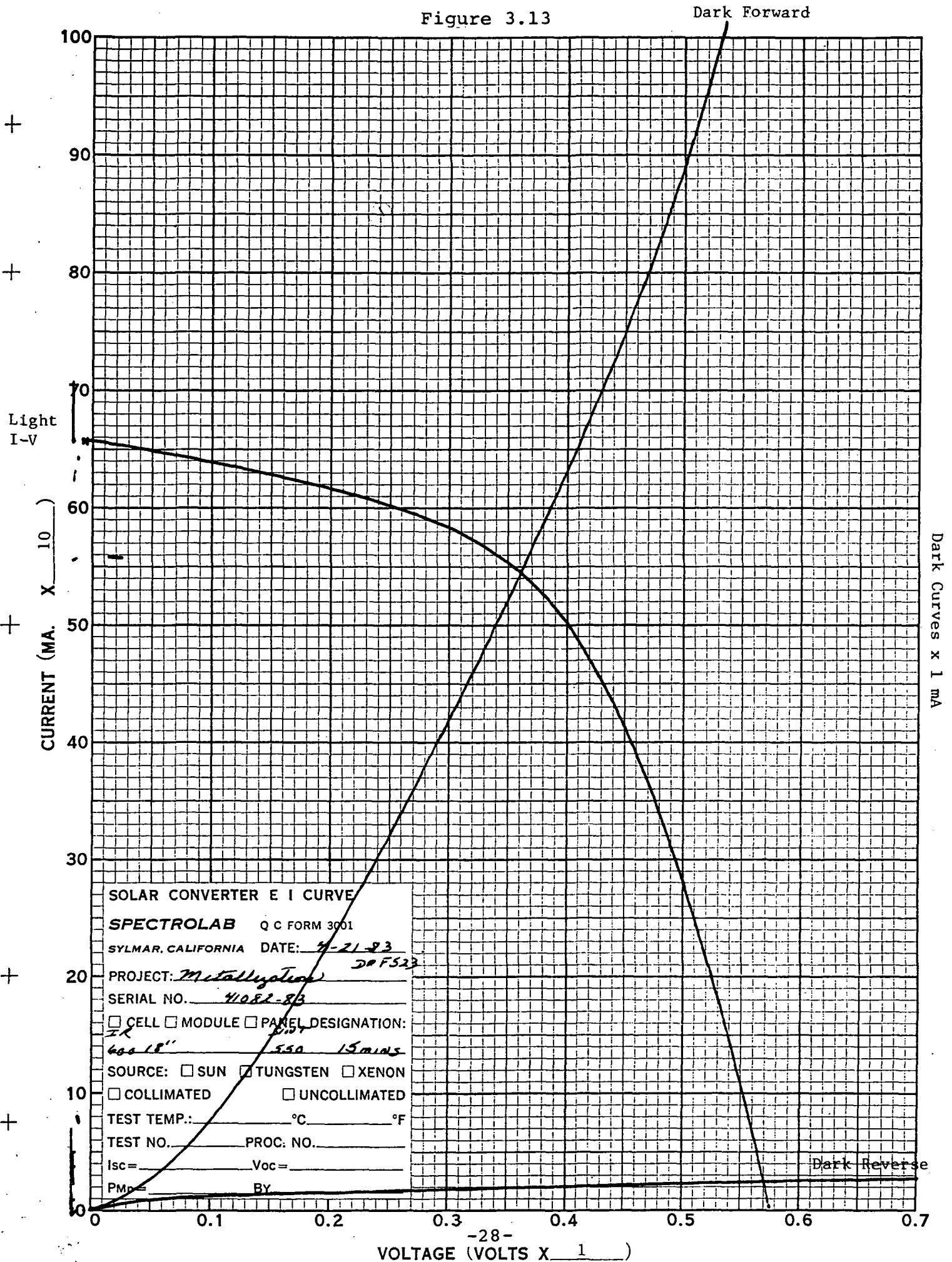


Figure 3.14

Dark Forward

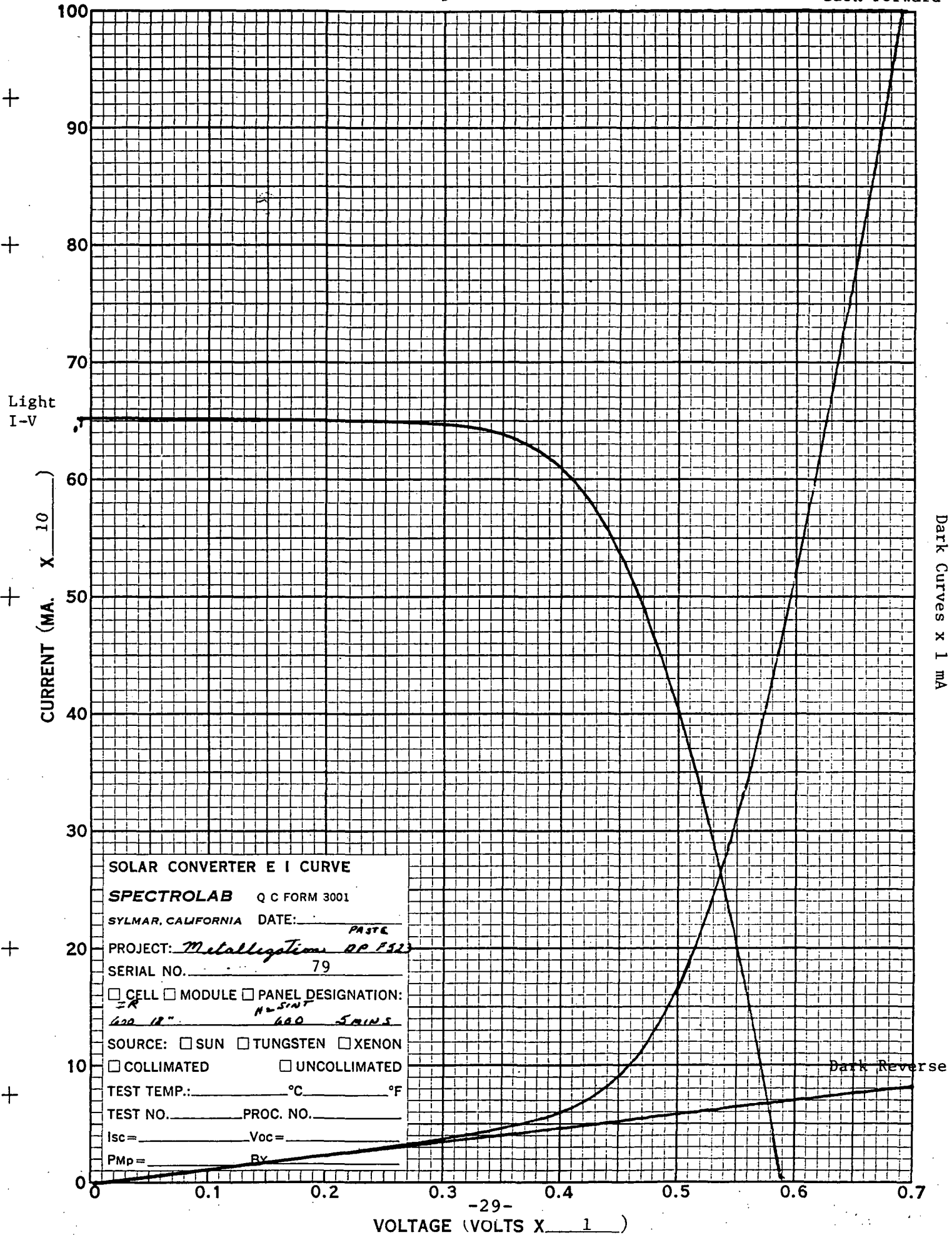


Figure 3.15

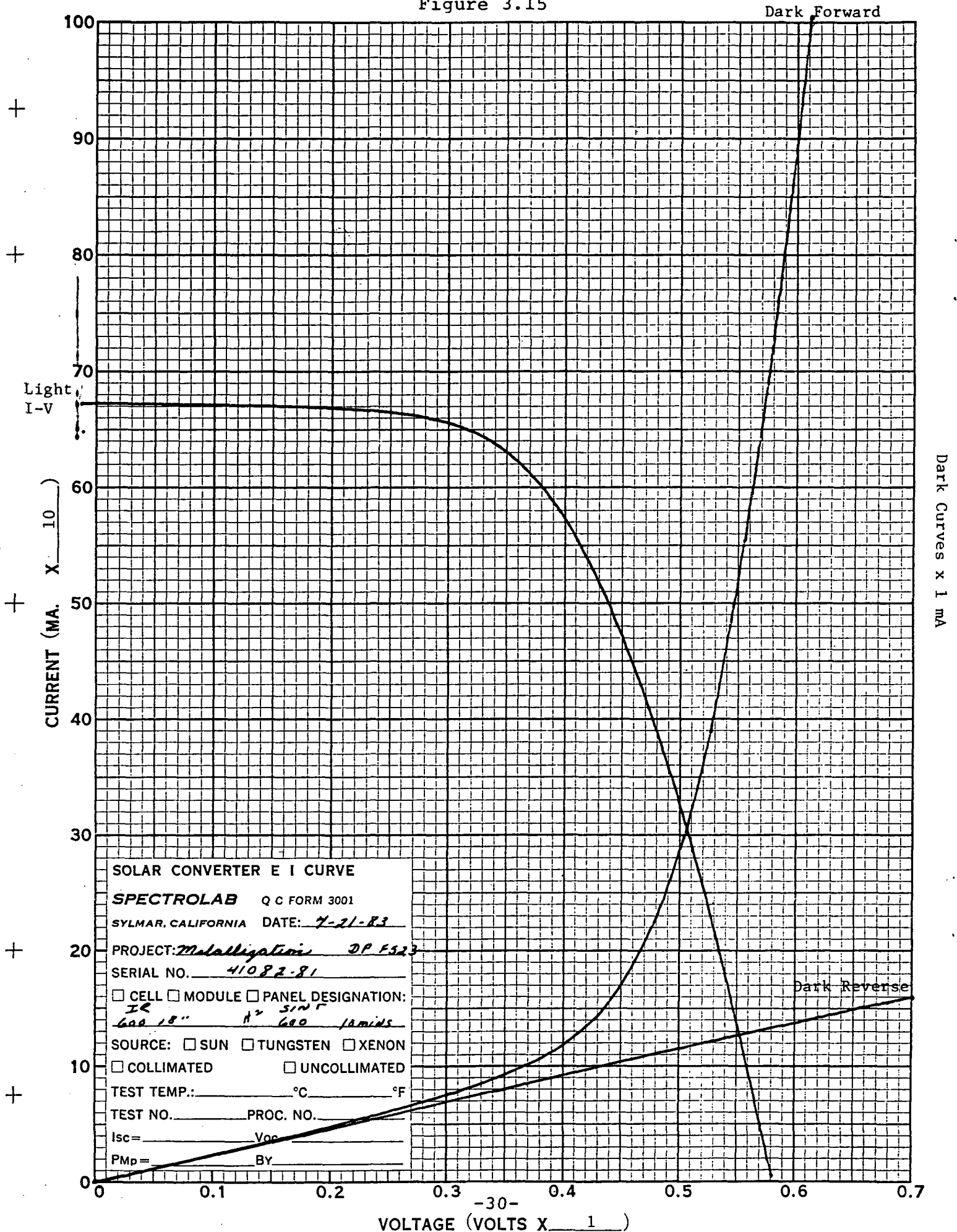


Figure 3.16

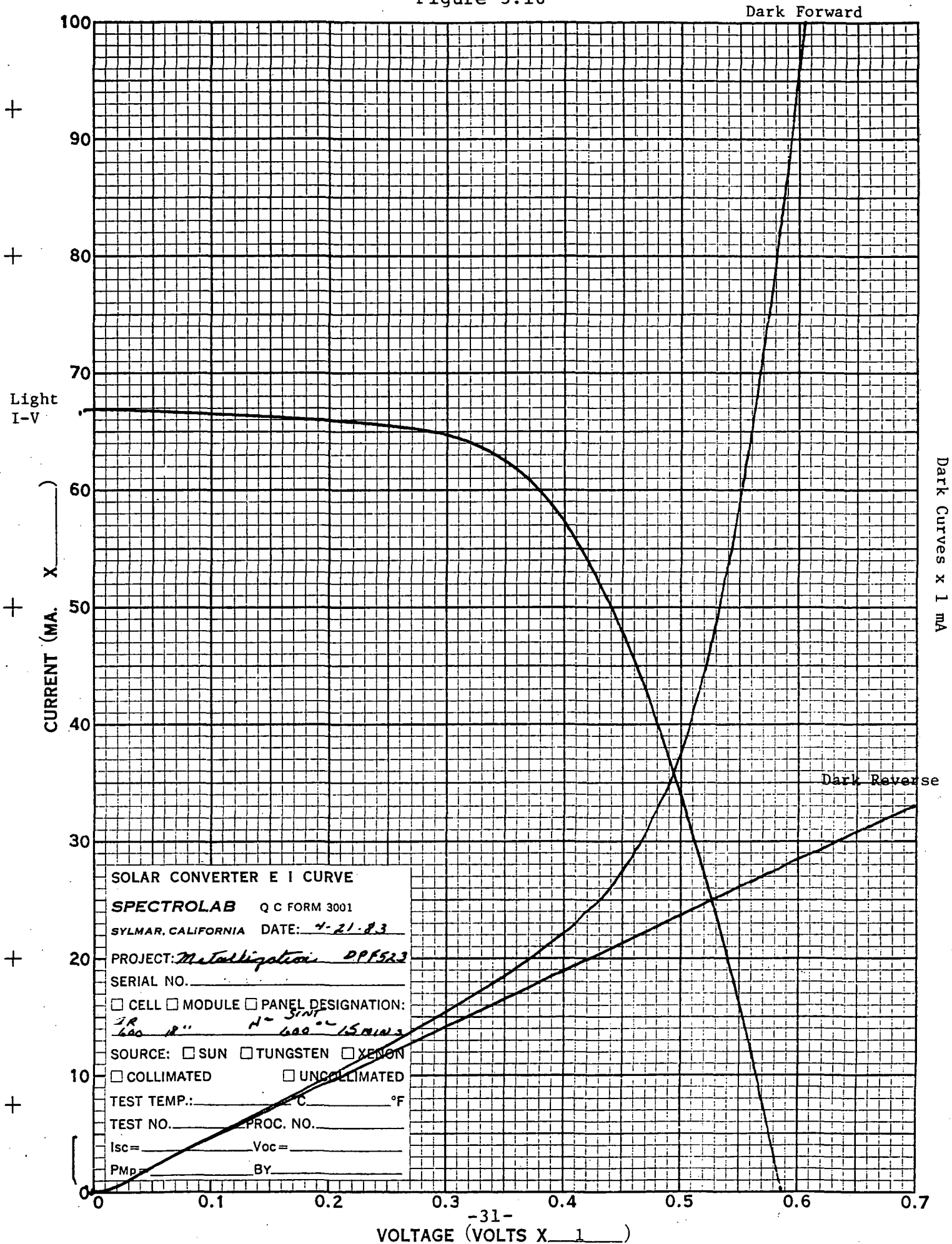
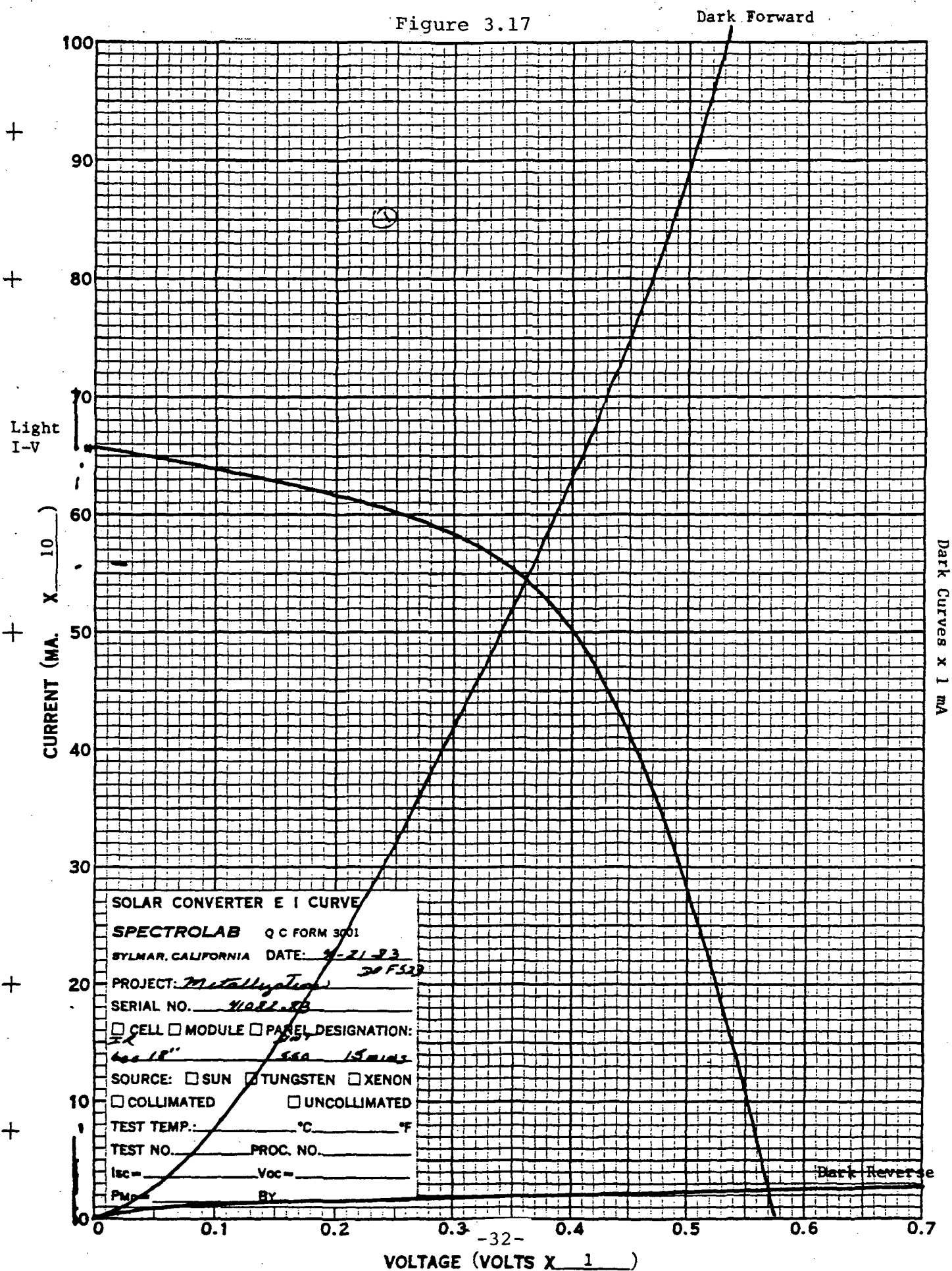


Figure 3.17



ohmic continuity between the silver and Mo/Sn metallizations. The cell was then resintered several times for five minutes but continued to degrade. Figures 3.18 and 3.19 show typical cells. Sintering at higher temperatures destroyed the contact between the metallizations as is seen in Figure 3.20.

Figure 3.18

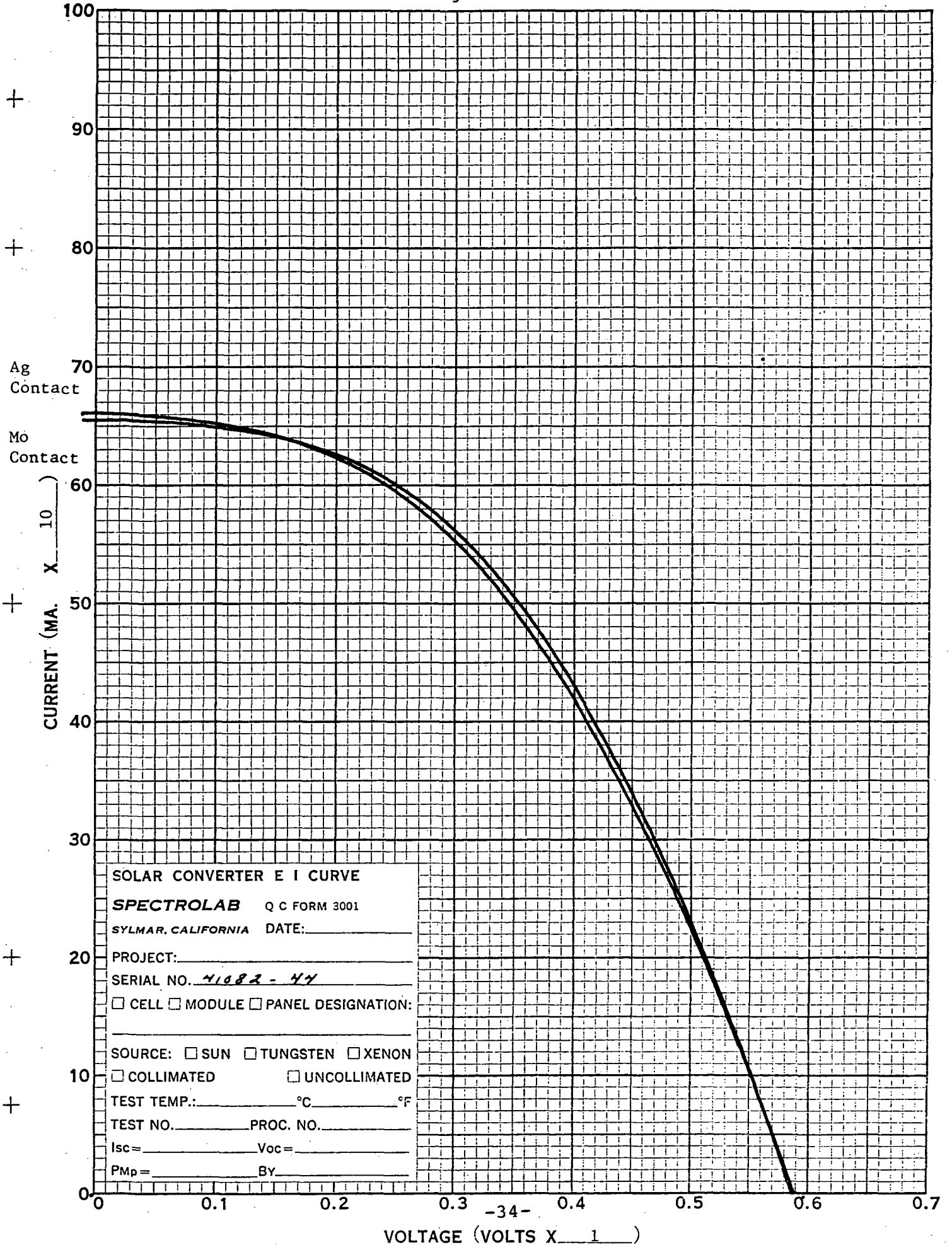
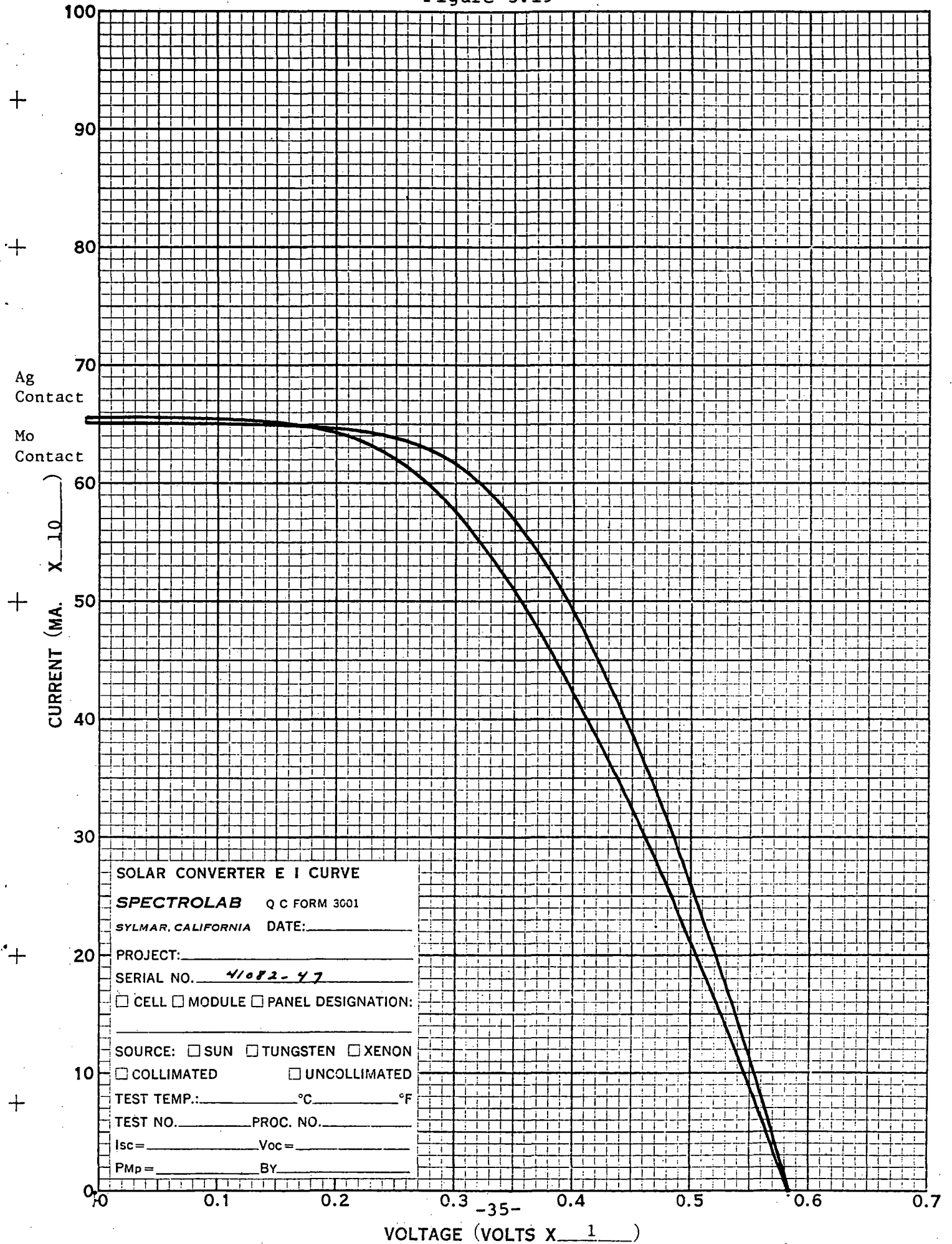
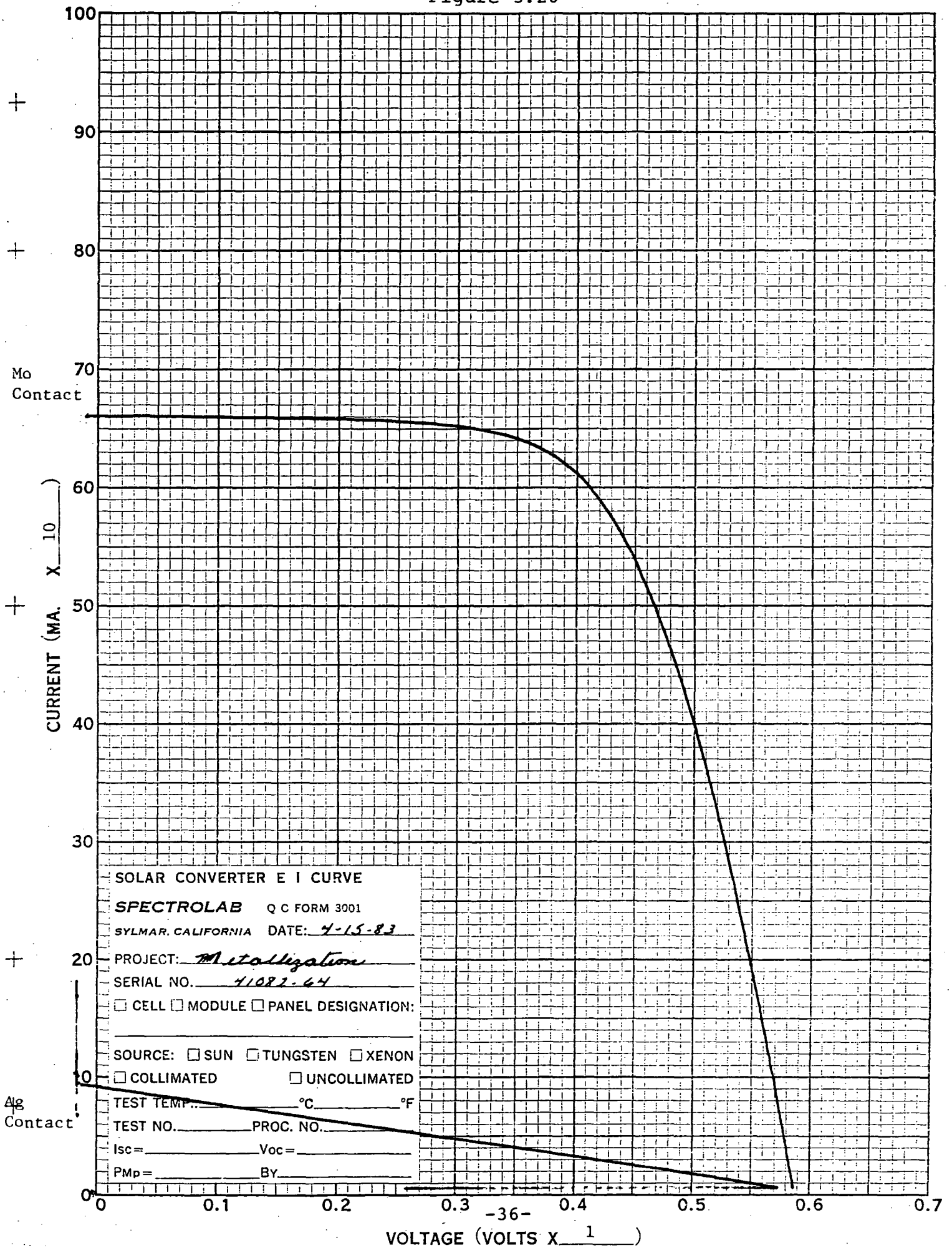


Figure 3.19



-36-



Section 4.0

ELECTRINK INKS

4.1 INITIAL MATRIX

Based on the problems encountered during soldering it was decided to do an extensive set of experiments with pastes using adhesion-enhancing additives. Electrink was chosen as the vendor for these additional pastes because they would supply complete compositional analyses of their pastes. Electrink also assisted in the formulation of experimental pastes. The following table summarizes the pastes:

Paste	Frit(Pb)	Frit 90	Frit 494	Teflon	V-26	V-38
A			X		X	
B			X	X	X	
C		X			X	
D		X		X	X	
E			X			X
F			X	X		X
G		X				X
H		X		X		X
I	X				X	
J	X					X
K					X	
L						X

The matrix of pastes includes three frit types: No. 90, No. 494, and No. 450. Table 4.1 shows the composition of the three frits. Frit No. 450 is a typical lead borosilicate frit similar to those used in silver pastes. The other two frits have no lead, one contains barium and strontium (#494), and one does not (#90). Two different vehicles are used in the pastes, a conventional cellulosic vehicle V-38 and an acrylic vehicle V-26. Table 4.2 shows the composition of the vehicles. Some formulations are also prepared with and without Teflon powder, and one without frit.

For the initial evaluation of the pastes, cells were made with and without prefiring the paste at 600°C. Cells that were not prefired were dried at 250°C. The cells were then fired at 600°C for 5 or 10 min. in H₂. Pastes E, I, J, and L gave the best results. Figures 4.1 - 4.5 show typical curves from these cells. All other pastes produced cells with no curve shape and short circuit currents less than 300 milliamps. Figure 4.1 shows the E paste prefired and then fired for 5 minutes at 600°C. The pre-fire was generally better than drying as is seen in Figure 4.2 where the cell was dried. Cells produced from pastes I and J are considerably worse with high series resistance as can be seen in Figures 4.3 and 4.4. Paste J had a Pb-borosilicate frit and should have produced results similar to the Thick Film System's paste A. This discrepancy may be due to differences in the frit or changes in the sintering oven at Spectrolab. Paste L (Figure 4.5) which contains no frit was comparable to E. In general the pastes with the cellulosic vehicle were superior. Pastes containing Teflon powder (B, D, F, and H) produced cells with no electrical output. Contact and series resistance measurements were made on several of the cells produced. The pastes were also printed on ceramic substrates to determine bulk resistivity more accurately.

Table 4.1

FRITS INVESTIGATED

	<u>#450</u>	<u>#90</u>	<u>#494</u>
K_2O	1.80	0.41	2.20
Na_2O	2.36	6.33	2.03
CaO	5.98	13.97	9.35
MgO	0.32	0.76	0.41
PbO	31.72	-	-
Al_2O_3	3.50	9.75	5.09
B_2O_3	13.76	13.92	7.99
SiO_2	40.56	54.86	55.66
SrO	-	-	6.08
BaO	-	-	11.19
$MP^{\circ}C$	827	843	771

Table 4.2

VEHICLE FORMULATION

	<u>V-38</u>	<u>V-26</u>
α -Terpineol	43.62	88.00
Butyl Carbitol Acetate	43.62	
Ethyl Cellulose N-14	9.76	
Thixatrol ST	3.00	
Elvacite 2042		9.00
Troykyd XYZ		3.00

Figure 4.1

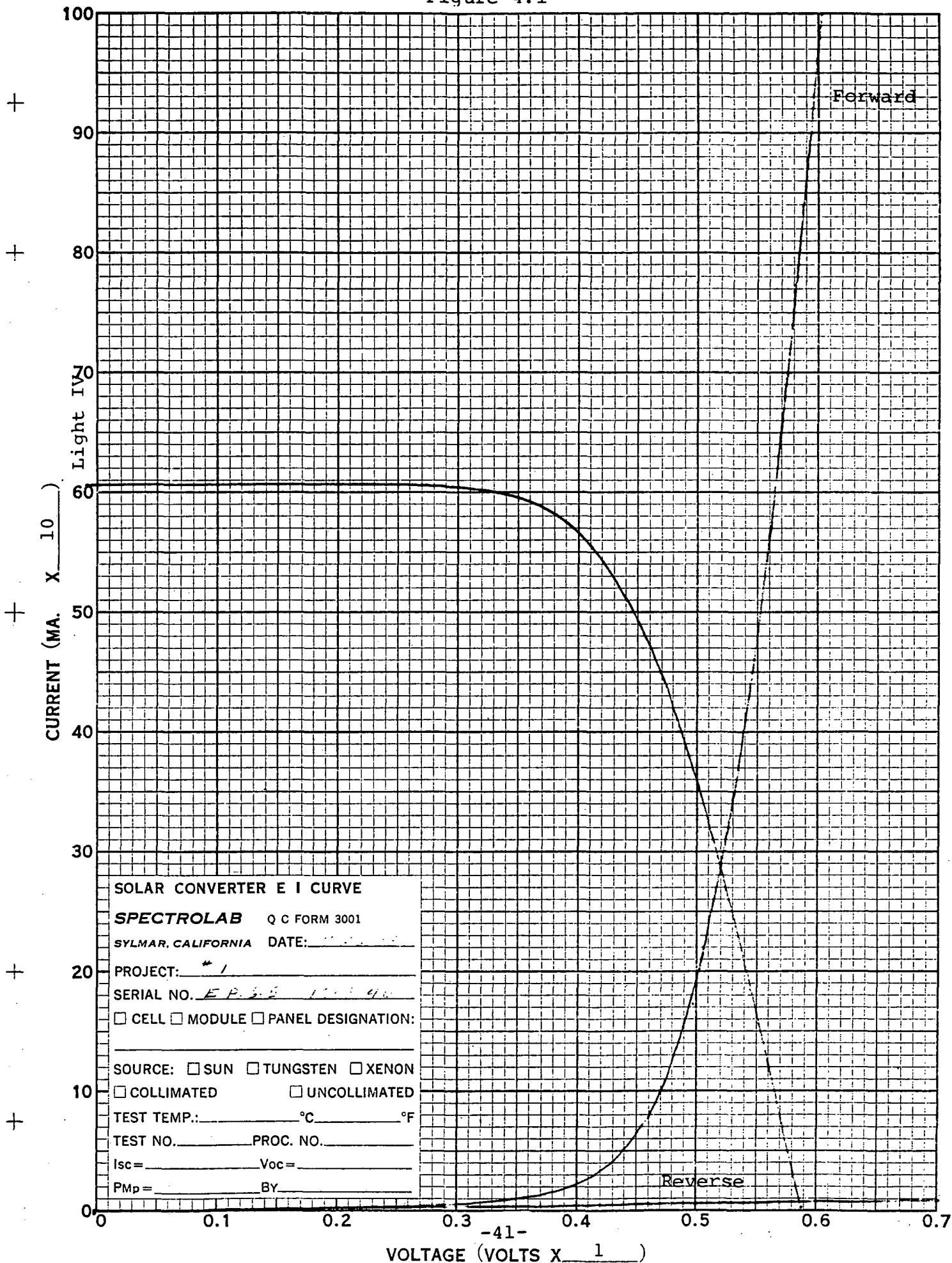


Figure 4.2

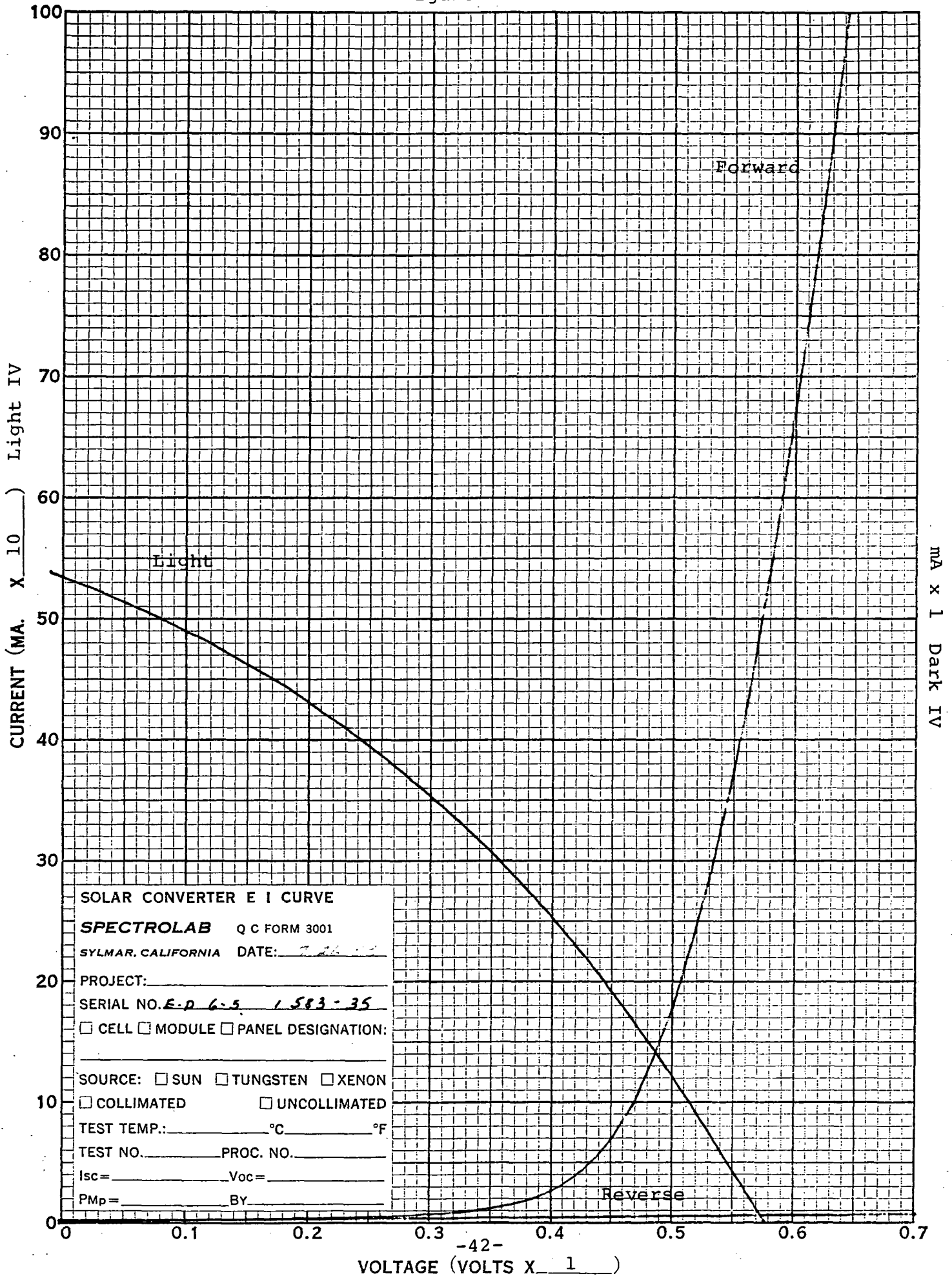


Figure 4.3

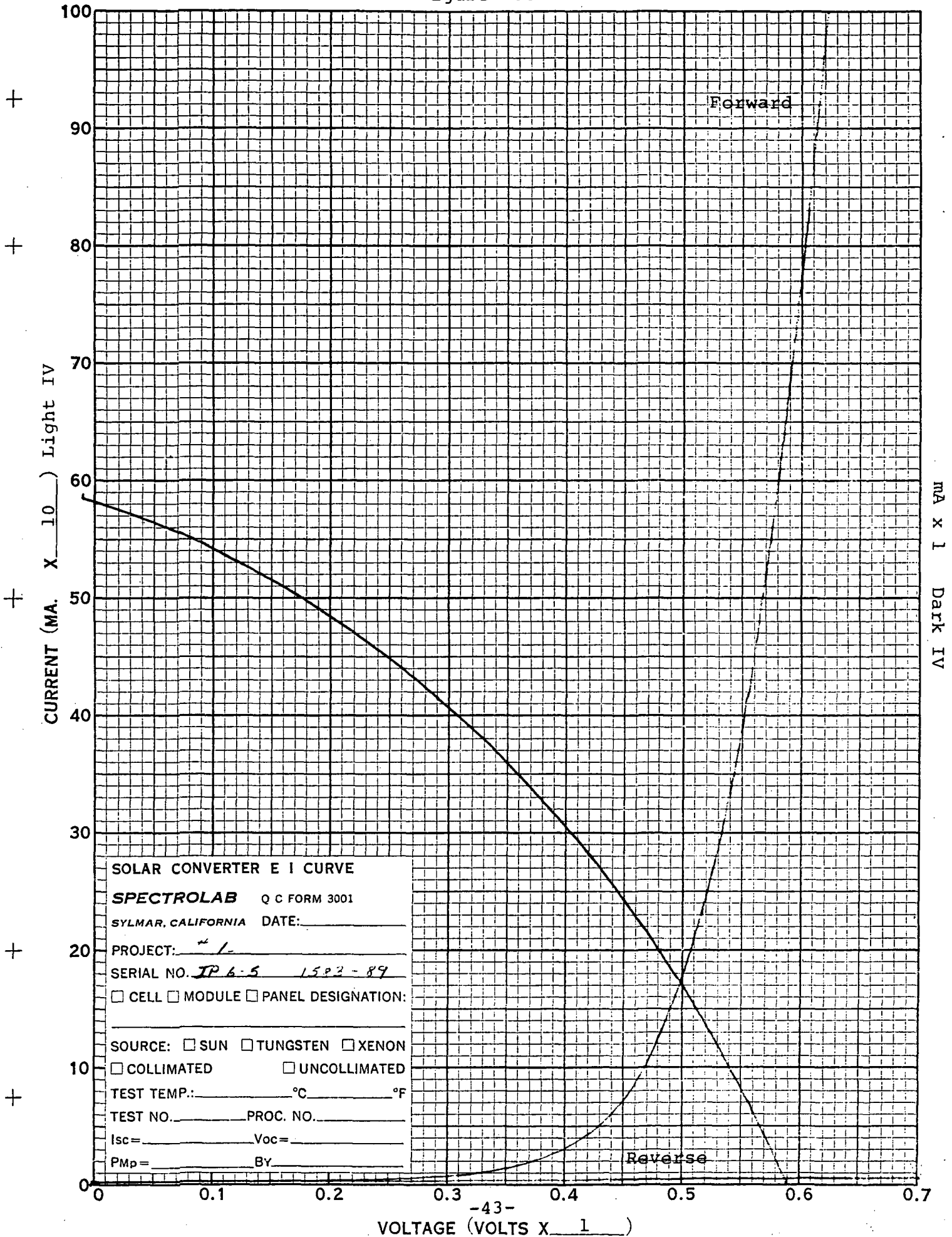


Figure 4.4

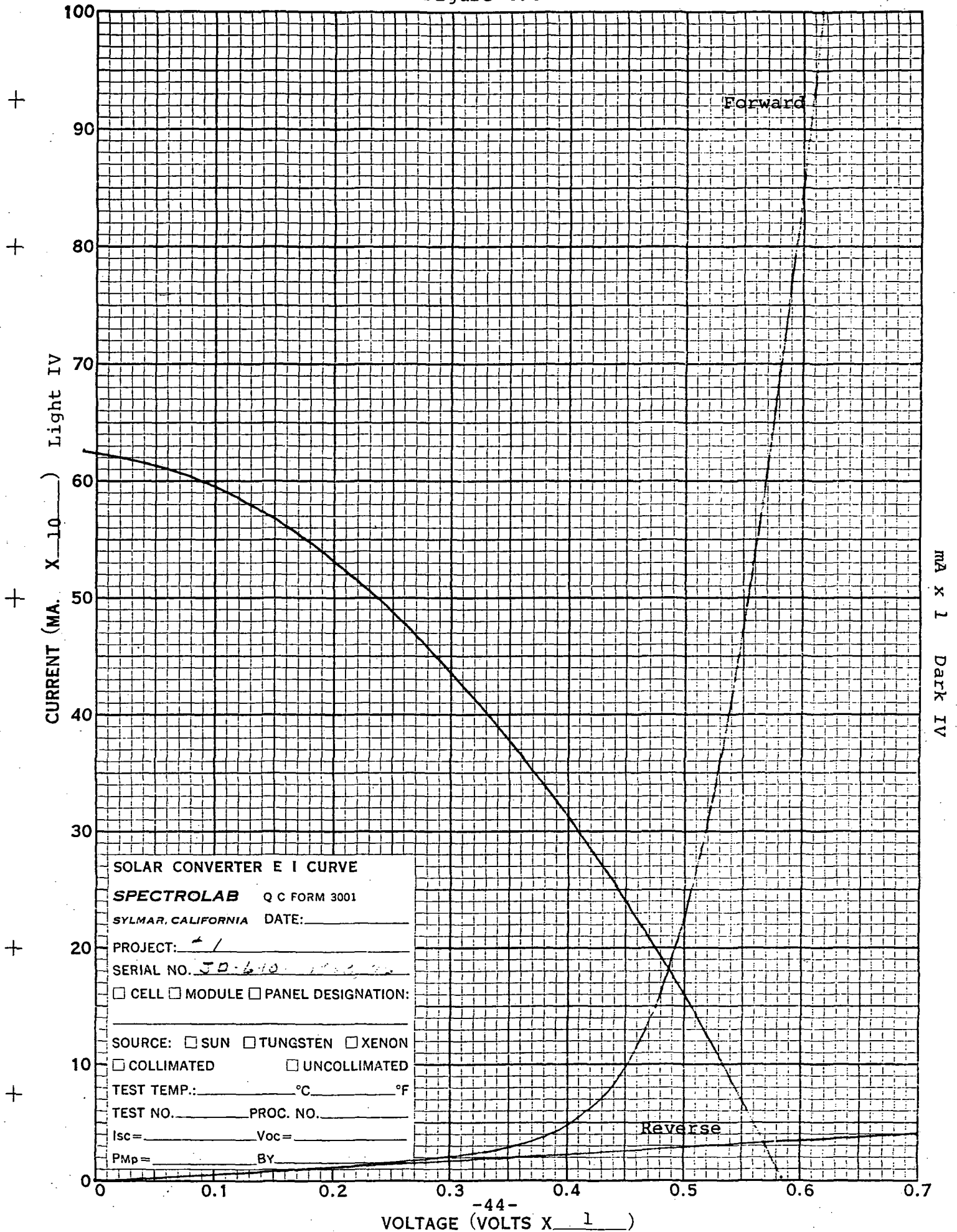
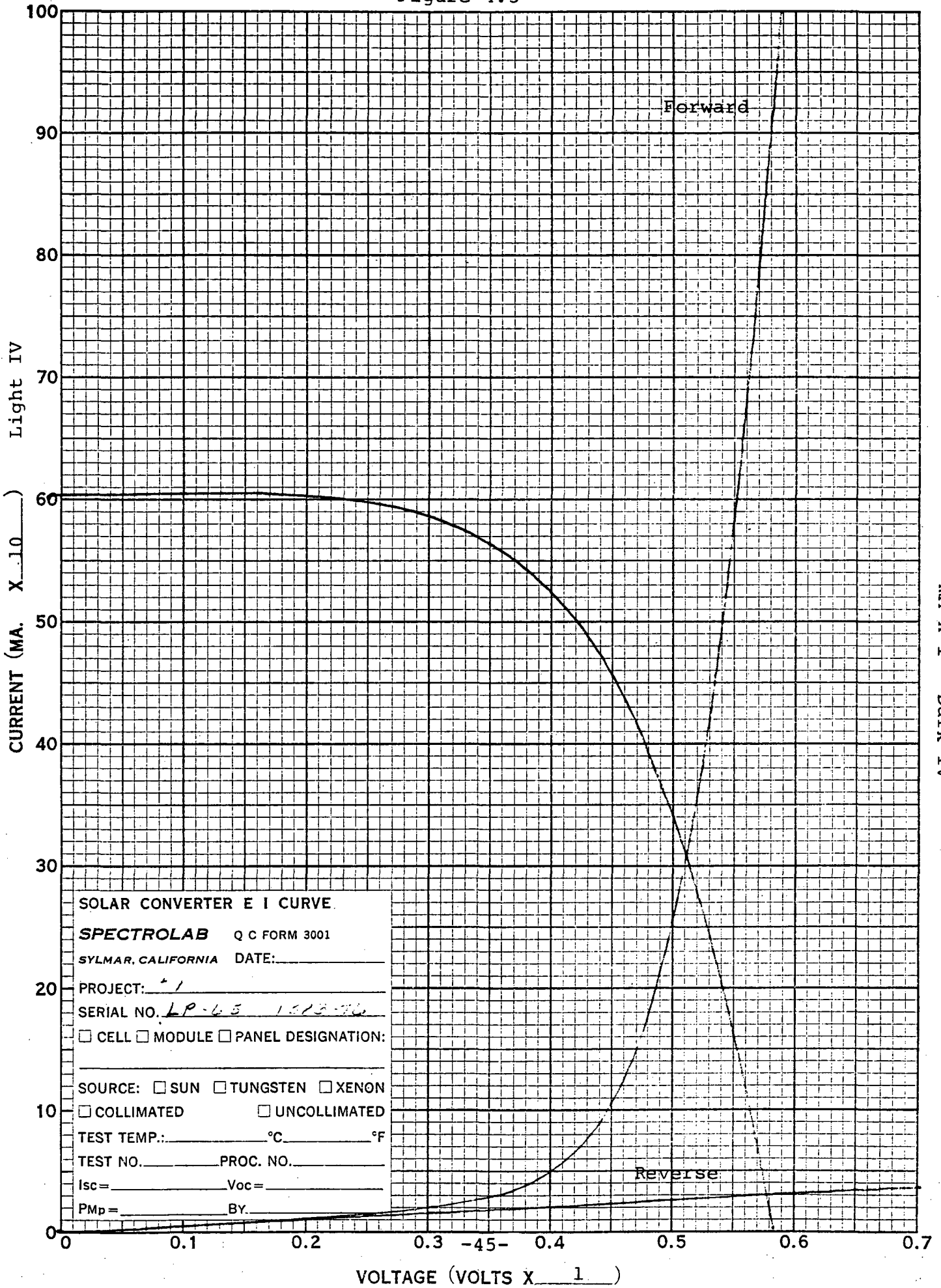


Figure 4.5



Contact resistance was measured by dicing the cell into nine equal sections. This cutting creates sections which have six equivalent unconnected sections of metallization. By measuring the voltage drop at constant current (10 mA) between the outermost section and the other sections, a graph can be created as shown in Figure 4.6. The following equation applies to the graph:

$$V/I = nR_B + 2R_C$$

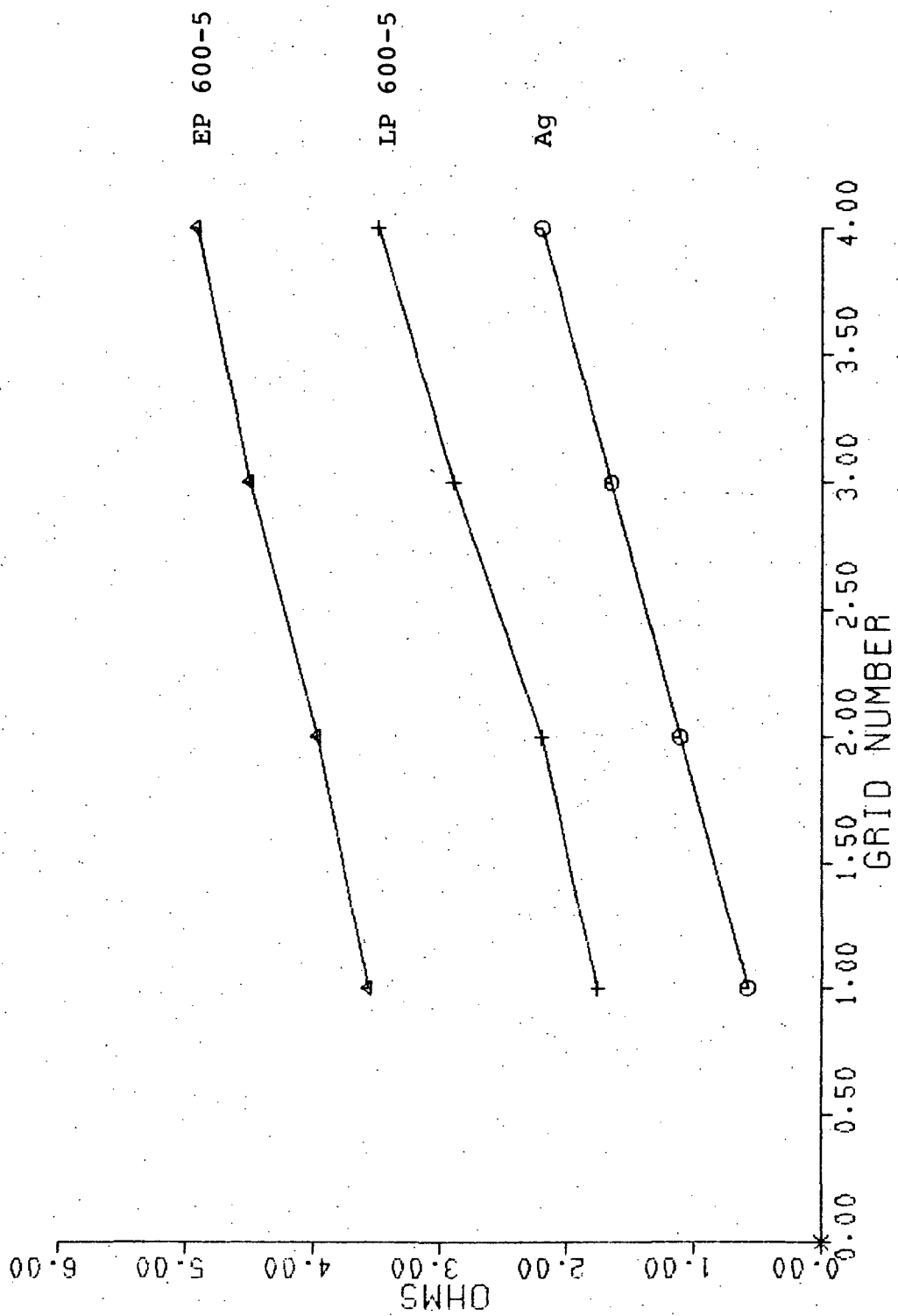
where

- V = the measured voltage drop
- I = the current (10 mA)
- n = the grid number
- R_B = a bulk resistance between grids
- R_C = the contact resistance for the grid contact area

The y intercept of this line represents the contact resistance over the contact area of a single section. The contact area on these samples was 0.68" x the grid width measured by profilometry. This quantity is not exact when the bulk resistivity of the metallization approaches that of the underlying silicon. that condition may occur in poorly sintered samples. Therefore the quantities determined must be used for relative, not absolute, measurements. Bulk resistivity was determined using a four point probe measuring voltage drop along a grid line. Measurements were also made on samples made using ceramic wafers in place of silicon. These samples did not turn out well due to the different thermal characteristics of the ceramic material. The time was not taken to optimize the ceramic firings. The cross section area of the grid lines was then measured using a profilometer. Figure 4.7 shows typical data from this device. The accurate determination of cross sectional areas of the grid lines is

Figure 4.6

CONTACT RESISTANCE



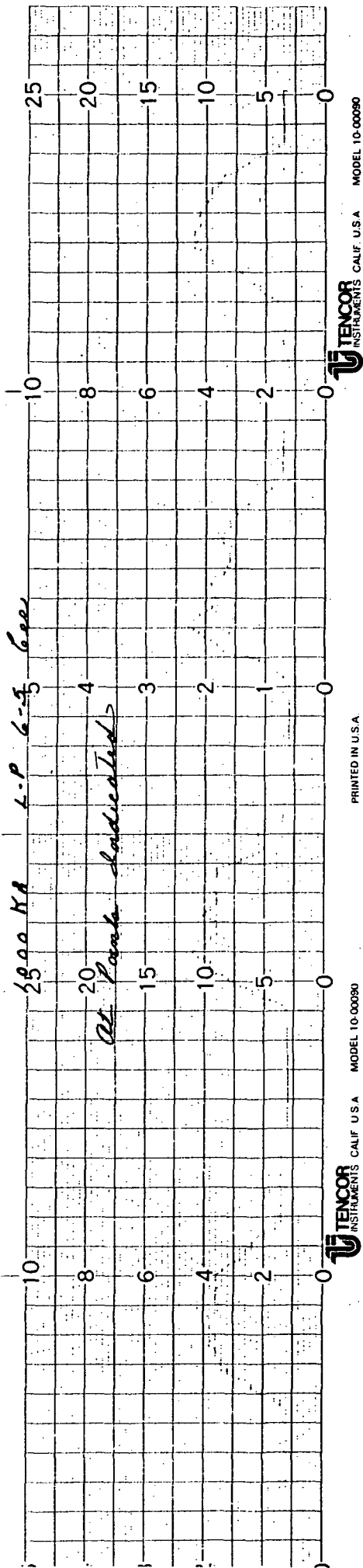
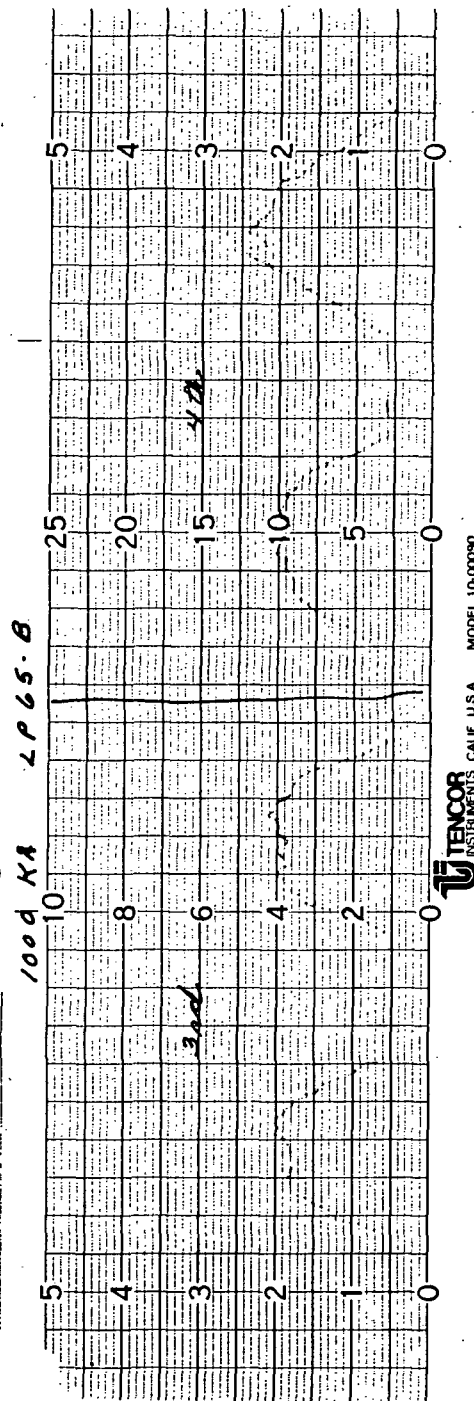
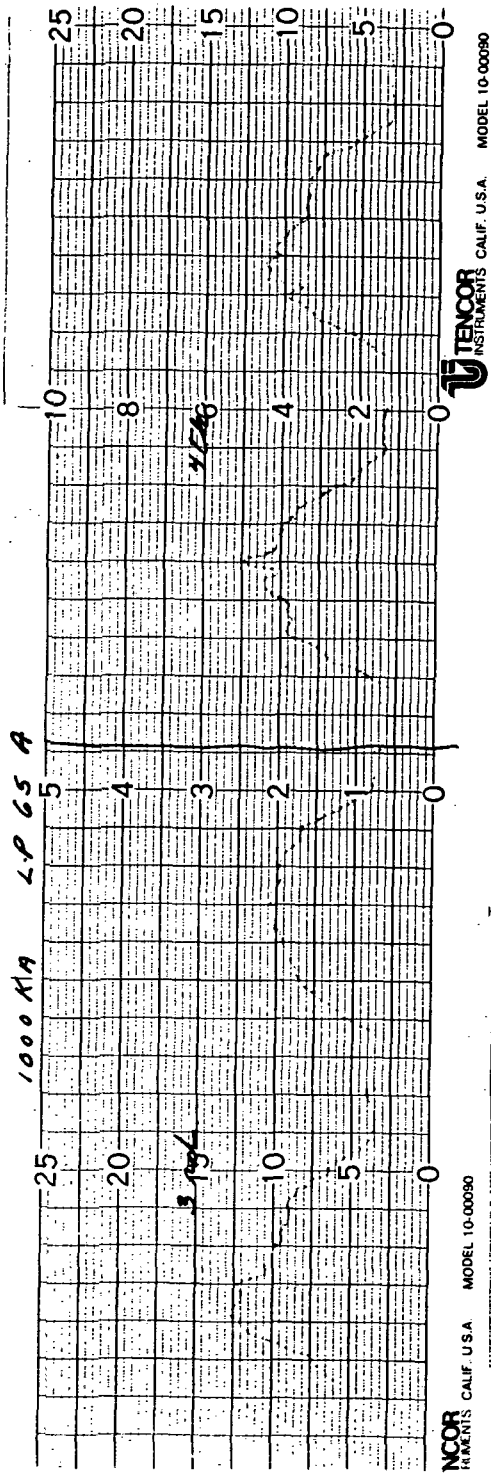


Figure 4.7
PROFILOMETER
DATA

difficult if not impossible due to the irregularity in grid profiles. Thus resistance values determined must be viewed with caution. Using the cross section area and the calculated resistance the bulk resistivity can be determined. This number is accurate when the resistivity of the metallization is much less than that of the layer beneath it. The value of resistivity will be lower than is correct when the metallization value approaches that of the substrate. Table 4.3 showed the results of bulk and contact resistivity measurements. The values that are measured on silicon should only be used for relative, not absolute, comparisons.

JPL took several SEM micrographs of various sintered cells to investigate changes that have been made in sintering process parameters. These analyses make it clear that most cells were not being sufficiently sintered. Changes were then made in the hydrogen delivery system for the sintering furnace to allow the flow of H₂ to be increased 7 fold to 2.5 l/min. Repetitions of earlier runs were made using pastes E, I, J, and L. Cells were sintered for 5 or 10 minutes at 600°C in hydrogen. Paste I showed no better results than previous experiments. Cells with fairly good curve shapes were made using pastes E, J, and L. The curves with the best shape are shown in Figures 4.8, 4.9, 4.10. Figure 4.11 shows a silver control cell for comparison. Electrical characteristics follow:

CELL	I _{sc}	V _{oc}	I ₅₀₀	EFF (if AR)
Ag	644mV	547mV	574mA	10.2% (13.5)
76	652	569	524	9.6 (12.8)
70	620	579	320	7.6 (10.1)
88	606	580	255	6.6 (8.7)

Table 4.3

<u>Paste</u>	<u>Substrate</u>	<u>Prefire</u>	<u>Fire °C/Min.</u>	<u>Contact Resistance</u>	<u>Bulk Resistivity</u>
Ag	Silicon	-	Standard	0.003 ohm-cm ²	~10 microhm-cm
Ag	Ceramic	-	Standard	-	~20
E	Silicon	yes	600/5	0.15	~300
E	Ceramic	yes	600/5	-	4000+
E	Silicon	yes	600/10	0.14	~200
E	Ceramic	yes	600/10	-	~1000
E	Silicon	dry	600/10	0.21	~100
E	Ceramic	dry	600/10	-	~1000
I	Silicon	yes	600/5	0.20	~400
I	Ceramic	yes	600/5	-	Friable
J	Silicon	dry	600/10	0.20	~150
J	Ceramic	dry	600/10	-	~300
L	Silicon	yes	600/5	0.05	~200
L	Ceramic	yes	600/5	-	~200

Figure 4.8

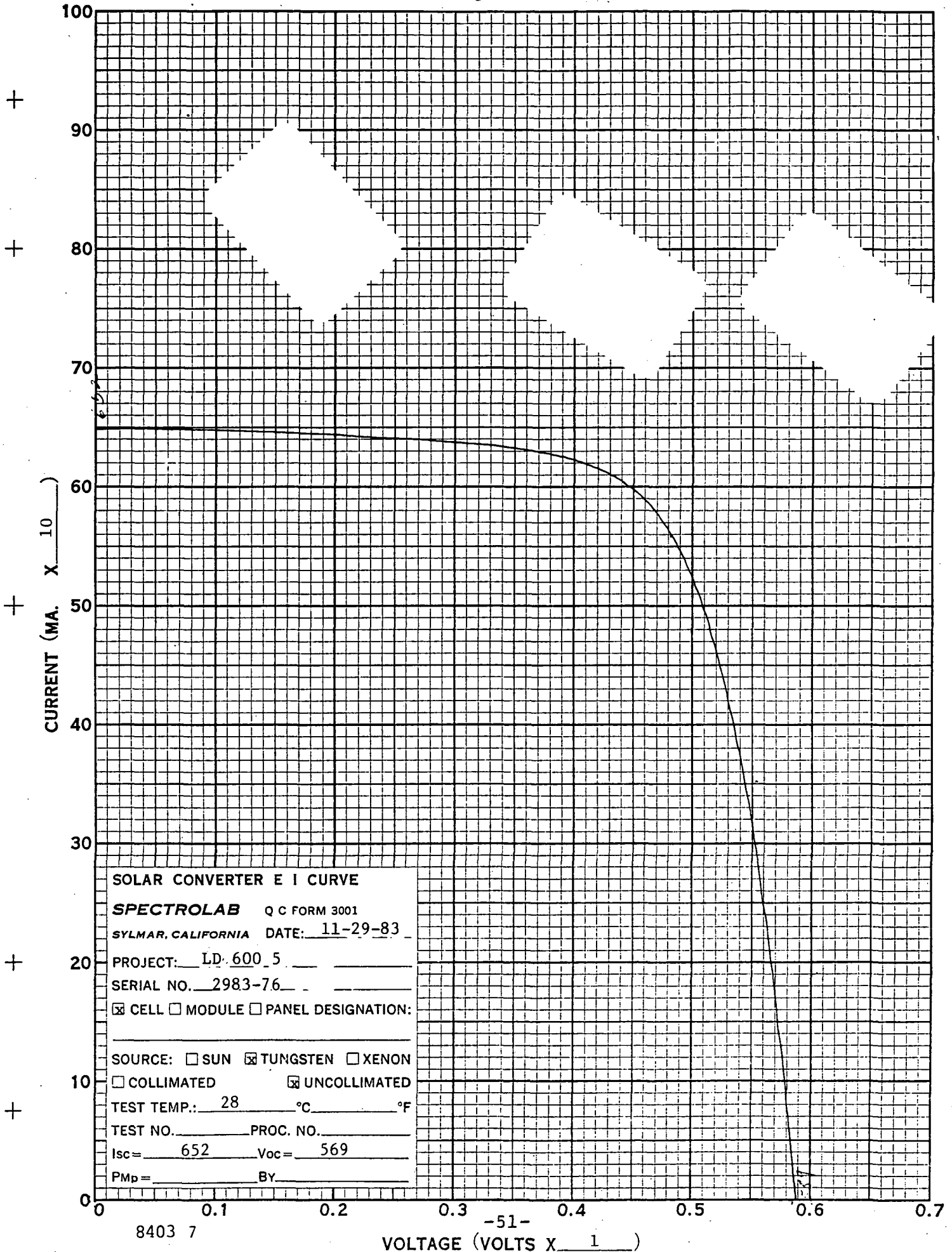


Figure 4.9

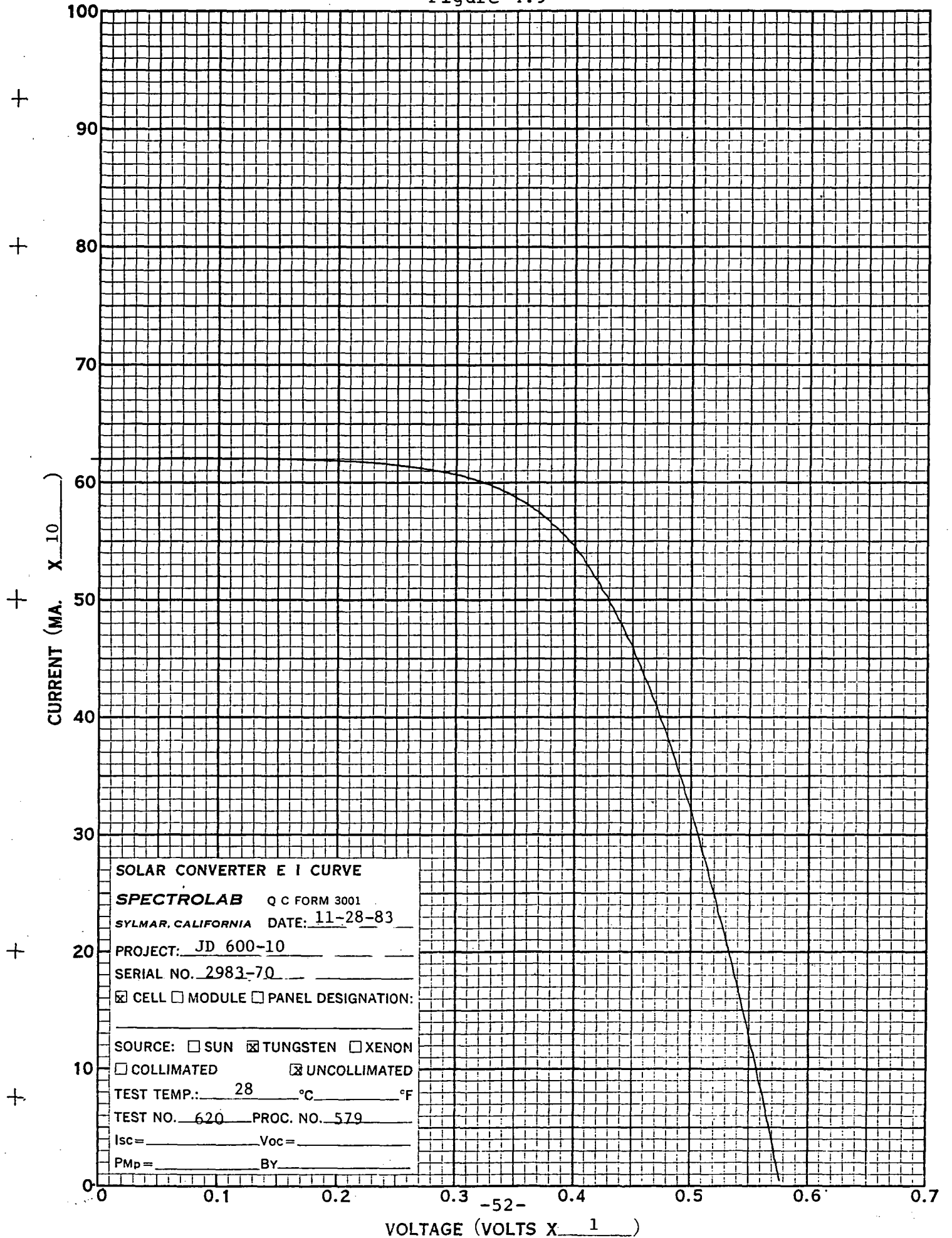


Figure 4.10

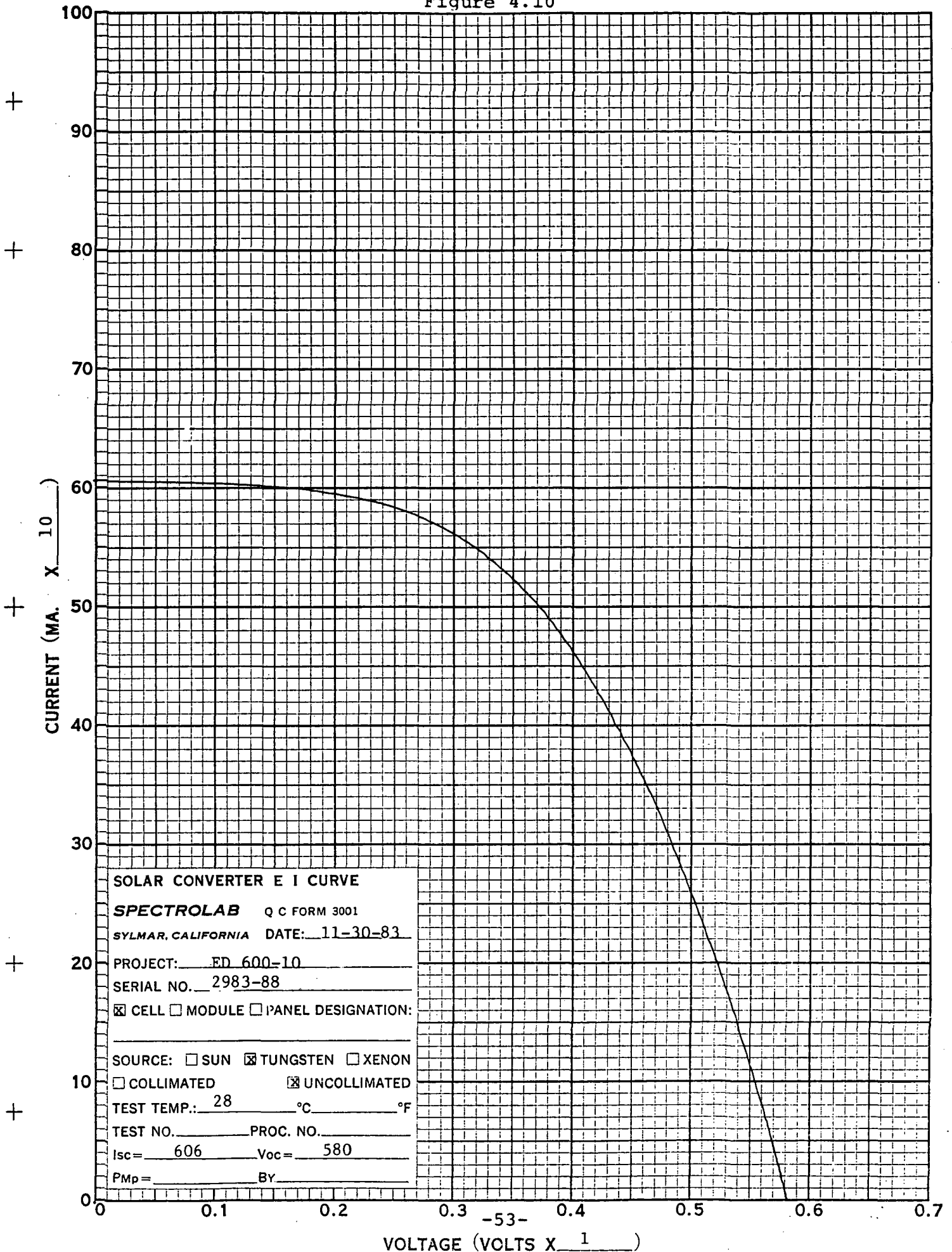
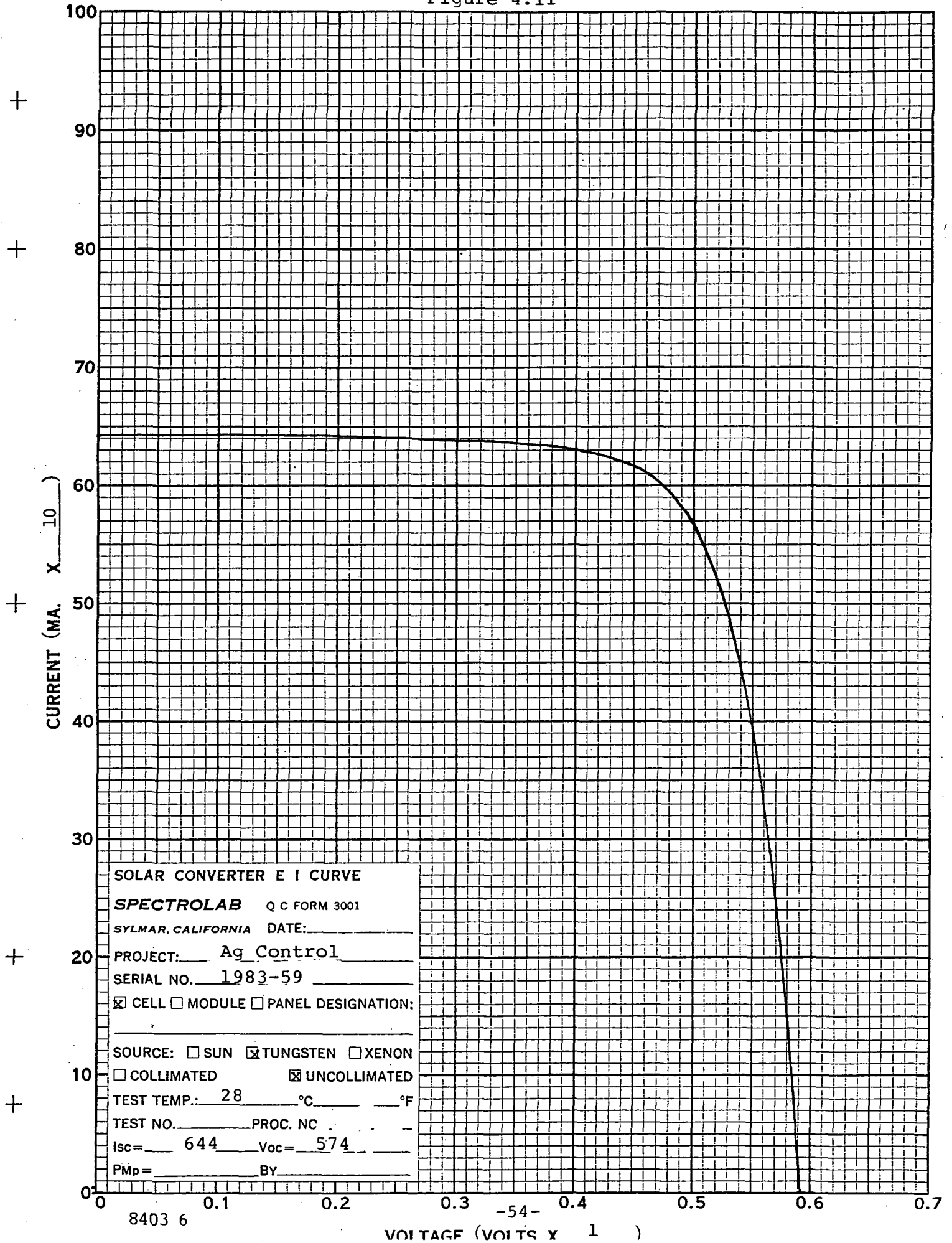


Figure 4.11



Loss of efficiency was caused by high resistance of the metallization in all cases. Shunt resistance was higher than that of the silver control.

Special sample holders were machined which will allow the non-destructive mounting of whole solar cells for SEM analysis. Figures 4.12 and 4.13 are SEM micrographs of an L paste cell at 500 and 2000 magnifications. These micrographs are typical of all the pastes. Sintering particle to particle is good. Where the Mo/Sn cell differs from the silver cell is in the wetting and contact to the silicon surface. Soldering of these cells confirmed this hypothesis in that a solder pull test removed the metallization as one piece leaving behind an unmarred silicon surface.

4.2 ADDITIONAL PASTES

Additional Pastes were procured from Electrink. Paste M uses MoO_3 in place of Mo metal with a titanium resinate and slightly different vehicle. Pastes N and O have boranepyridine added to a non-fritted paste. The formulations are shown in Tables 4.4, 4.5, and 4.6. A typical electrical curve of a cell produced using paste M is shown in Figure 4.14. The cells are fairly good electrically but not as good as the E, J, and L. cells. Solder results were equally poor. More work will be done using this paste to attempt to duplicate earlier successful research. Pastes N and O had borane-pyridine added to the nonfritted ink in 5% and 1% amounts. This was an attempt to produce a borosilicate frit in situ. The attempt was unsuccessful. All cells produced showed little or no electrical output due to extremely high series resistance. Additional cells were made using a modification of paste E. JPL supplied a solution of silver neodecanoate

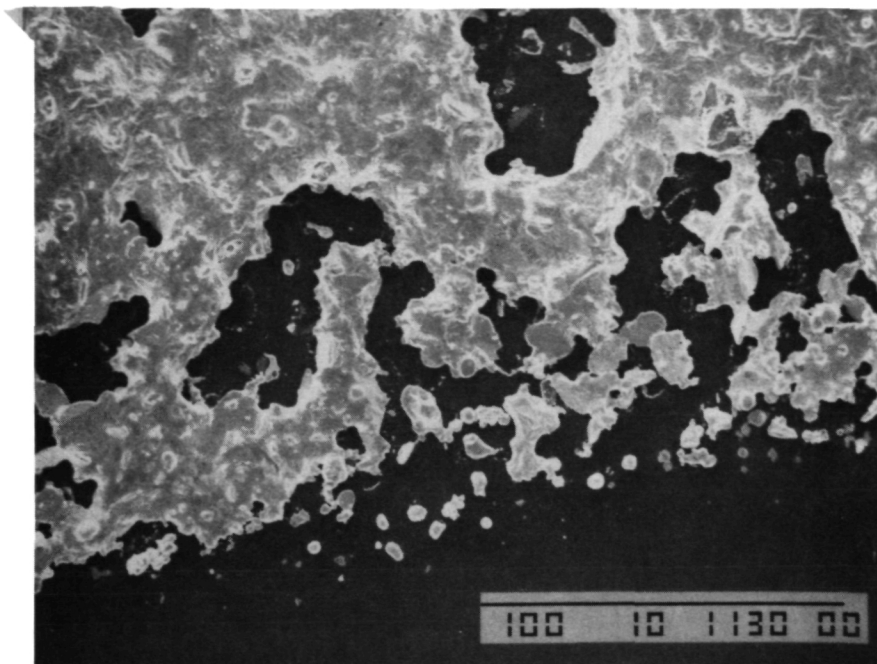


Figure 4.12

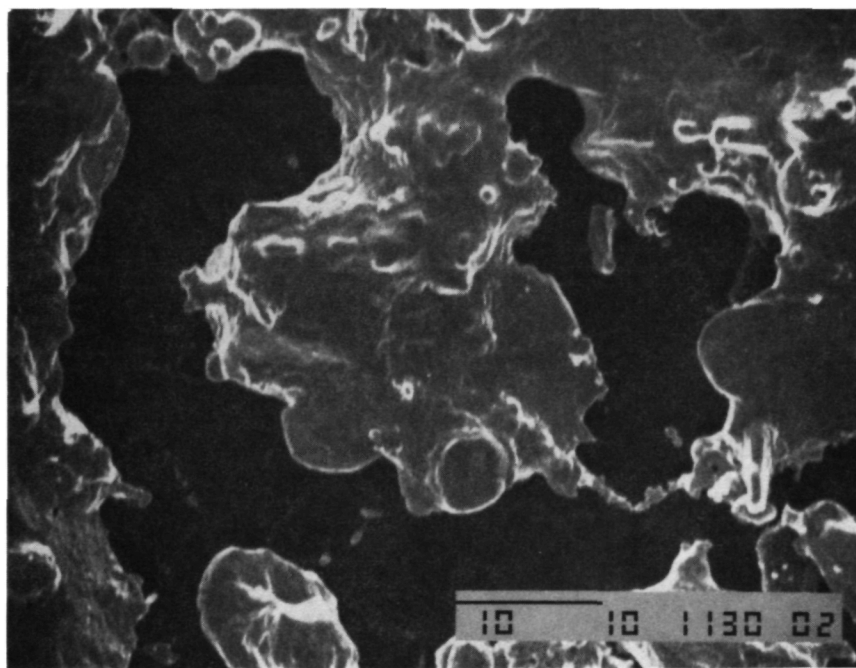


Figure 4.13

Table 4.4

PASTE M, ELECTRINK #F-82

FORMULATION

<u>Item</u>	<u>% by Weight</u>
Molybdenum Oxide (MoO_3)	17.572
Tin Metal Powder	64.907
Titanium Resinate	.002
Vehicle V-44	17.519

VEHICLE V-44

α -terpineol	70.54
Carbitol Acetate	4.17
Trichloroethylene	19.20
Ethyl Cellulose	6.09

Table 4.5

PASTE N, ELECTRINK #F-80

FORMULATION

<u>Item</u>	<u>% by Weight</u>
Titanium Hydride (TiH_2)	.45
Molybdenum Metal Powder	16.06
Tin Metal Powder	64.24
Borane Pyridine	5.00
Vehicle V-38	14.25

VEHICLE V-38

α -Terpineol	43.62
Butyl Carbitol Acetate	43.62
Ethyl Cellulose N-14	9.76
Thixatrol ST	3.00

Table 4.6

PASTE O, ELECTRINK #F-81

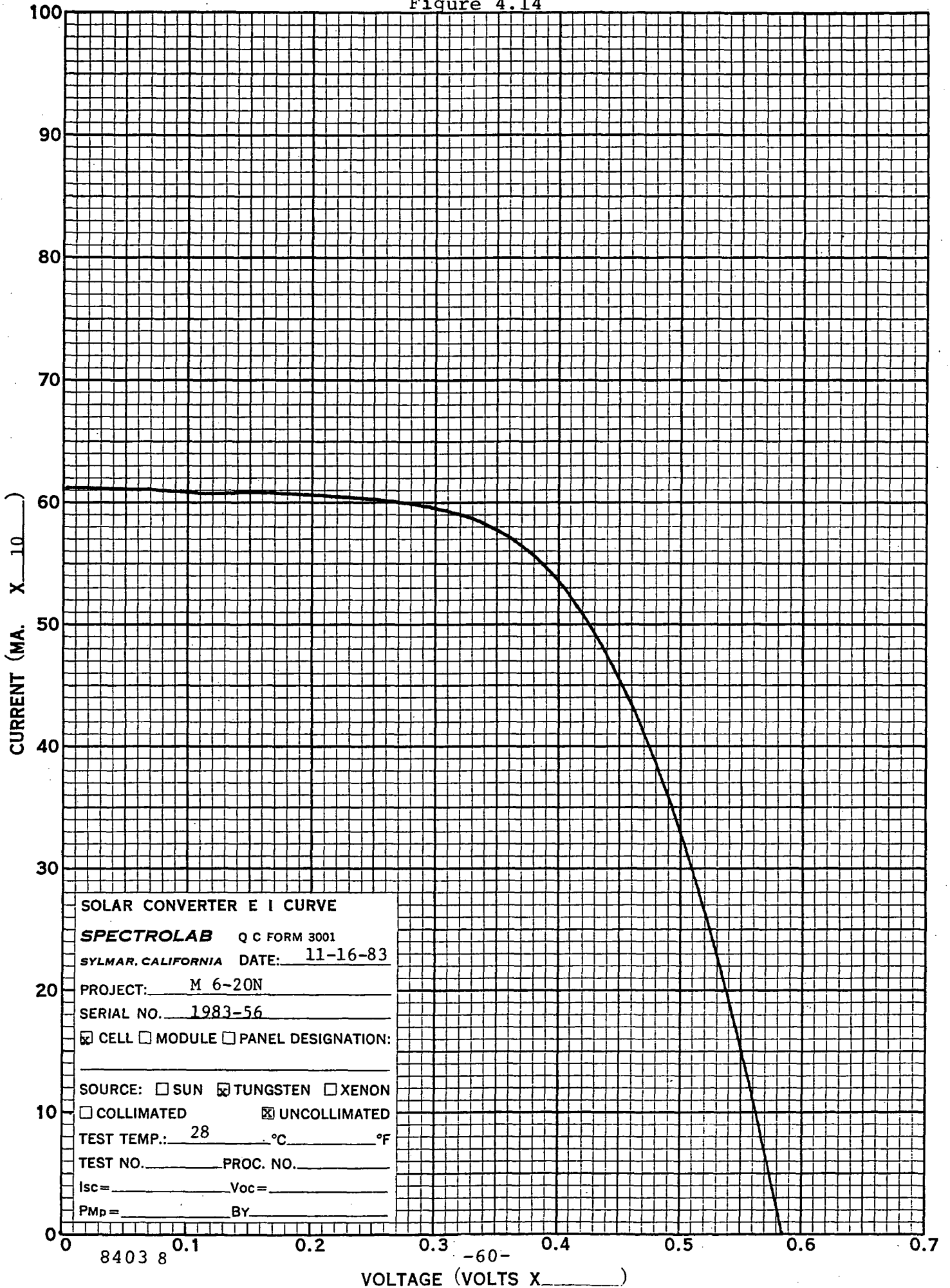
FORMULATION

<u>Item</u>	<u>% by Weight</u>
Titanium Hydride (TiH_2)	0.47
Molybdenum Metal Powder	16.73
Tin Metal Powder	66.92
Borane Pyridine	1.04
Vehicle V-38	14.84

VEHICLE V-38

α -Terpineol	43.62
Butyl (Arbitol Acetate)	43.62
Ethyl Cellulose N-14	9.76
Thixatrol ST	3.00

Figure 4.14



in xylene. The solution was 15% silver by weight. 4.3% of this solution was added to paste E. Wafers were screen printed and then either dried or prefired using the IR belt furnace. The cells were then fired in H₂ for 5 or 10 minutes. Figures 4.15 and 4.16 show cells made with and without the addition of the silver neodecanoate. The additive improved the curve shape but still did not impart adequate conductivity.

A series of experiments was done using pastes modified with indium resinate solution A2307 (Englehard-electro metallics, East Newark, NJ) and silver resinate solution 9144. Pastes E, J, and L were modified by adding 1% by weight of the resinates. The cells were processed as usual and then sintered at 650°C for 5 minutes in H₂. The J paste showed the best results with indium resinate added. Figures 4.17-4.20 show the light and dark IV curves for the best two cells using indium and silver resinates respectively. Further experiments using the J paste with indium resinate at higher sintering temperatures produced better cells. The best cell was produced by sintering at 700°C for 5 minutes. Figures 4.21 and 4.22 show the light and dark curves of this cell. The production of good cells using this process was not reproducible; about half of the cells produced were shunted as is shown in Figures 4.23 and 4.24. The better cells were still not solderable. Attempts to fine tune times and temperatures of sintering were not successful.

Three additional pastes were received from Electrink formulated using silver neodecanoate. The formulations are shown in Table 4.7. An extensive matrix of experiments using a prefire belt speed of 18-54"/min. at 400°C and sintering temperatures of 500-700°C was unsuccessful. The best cell is shown in Figures 4.25 and 4.26. Additionally sintering was attempted by simple

Figure 4.15

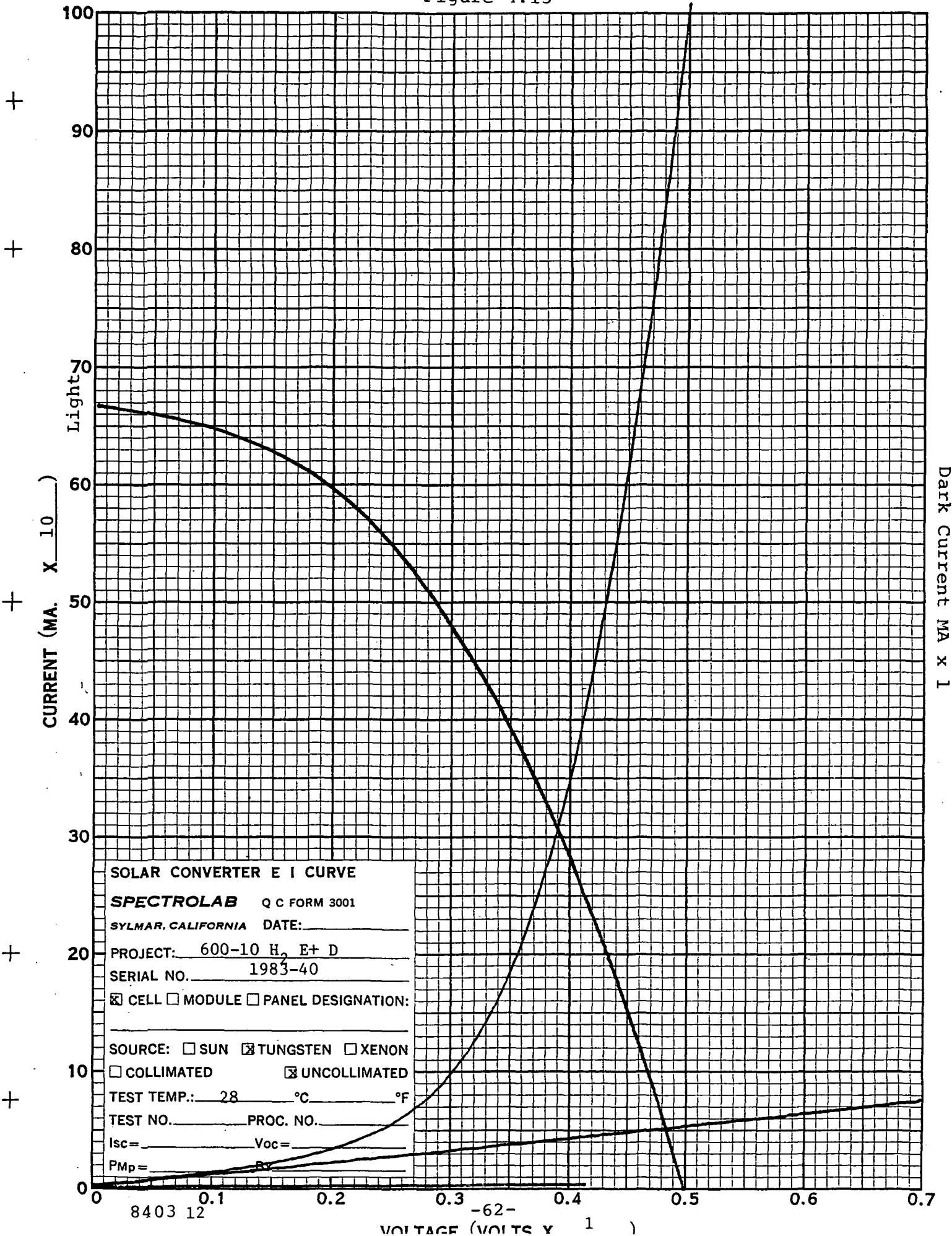


Figure 4.16

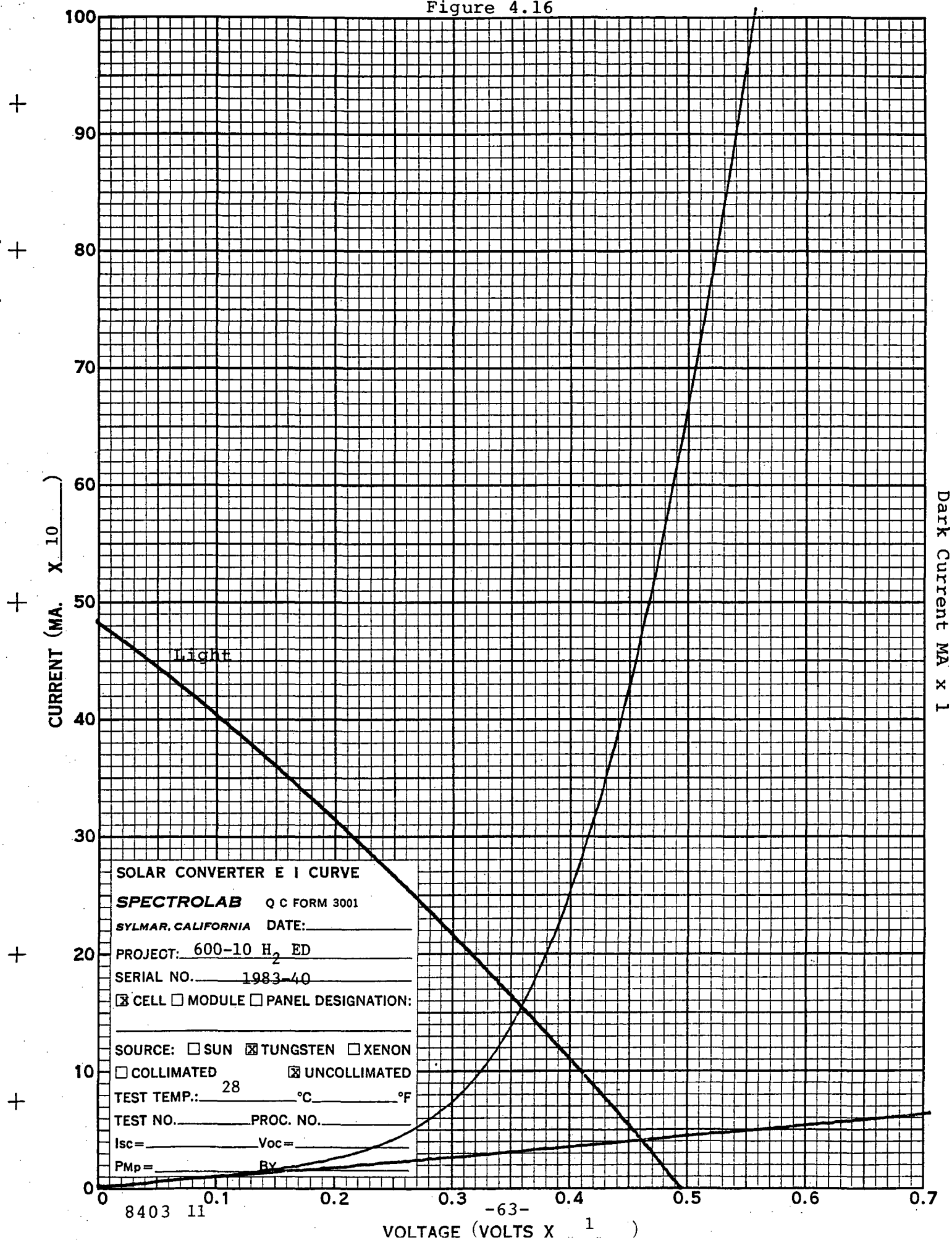


Figure 4.17

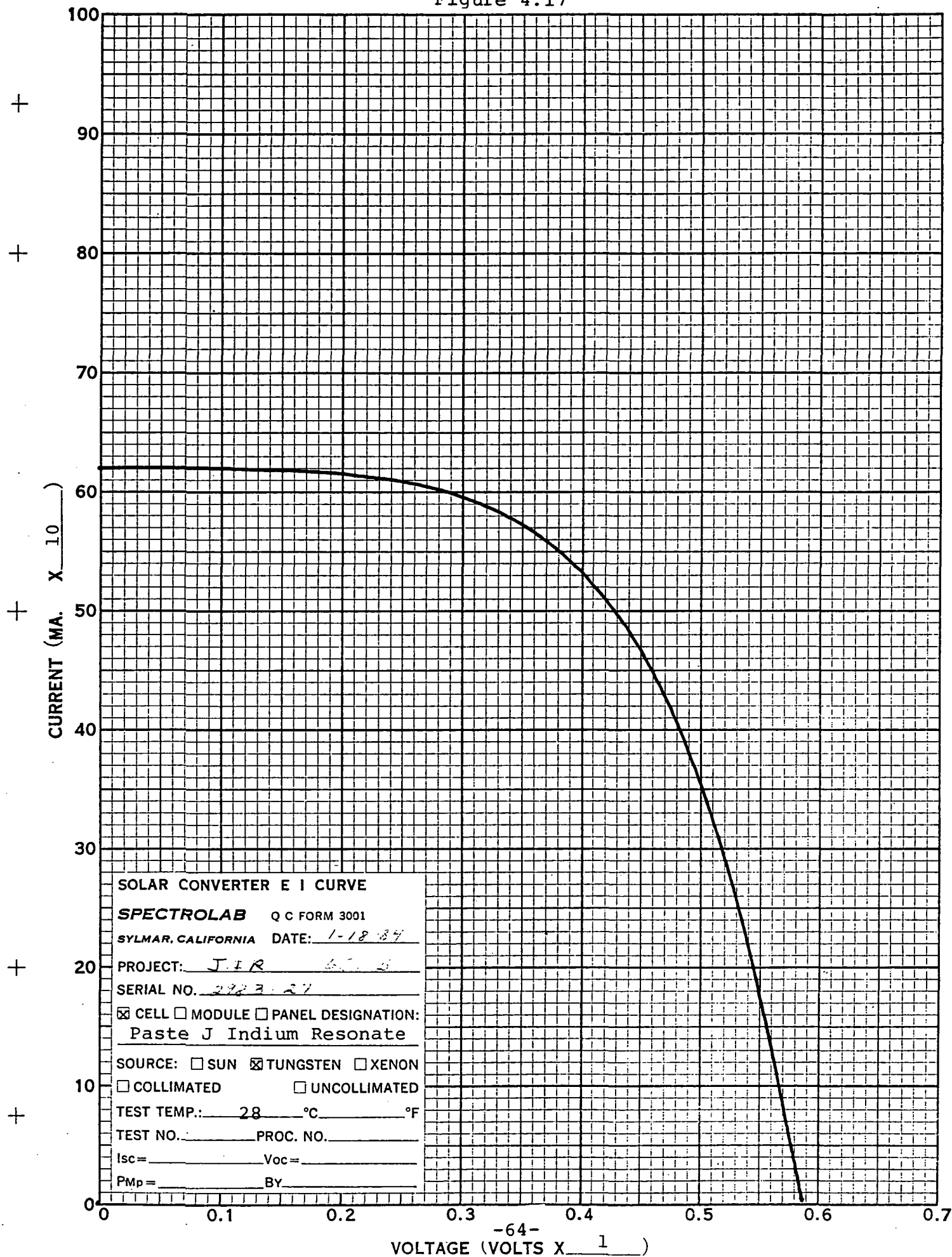


Figure 4.18

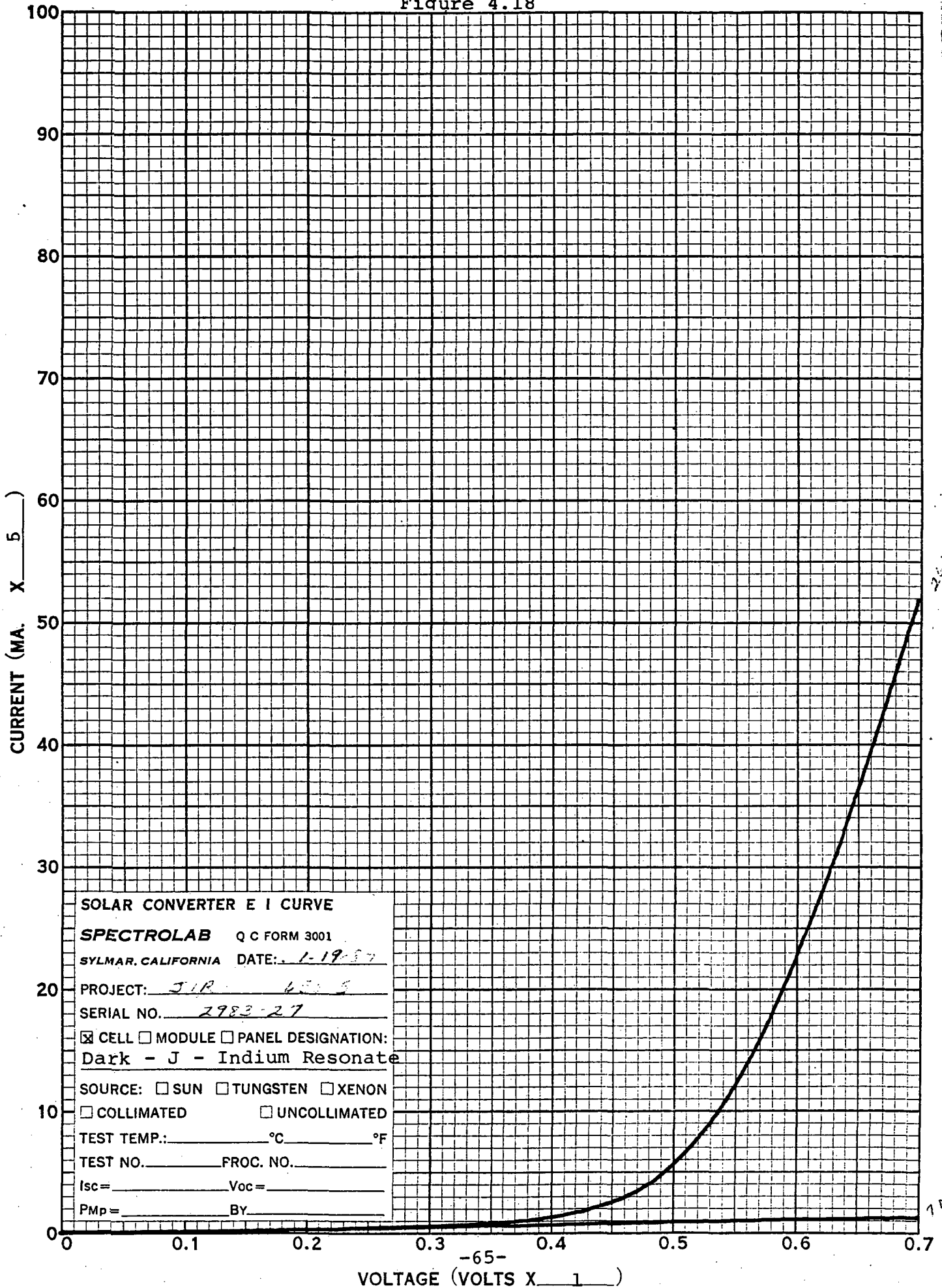


Figure 4.19

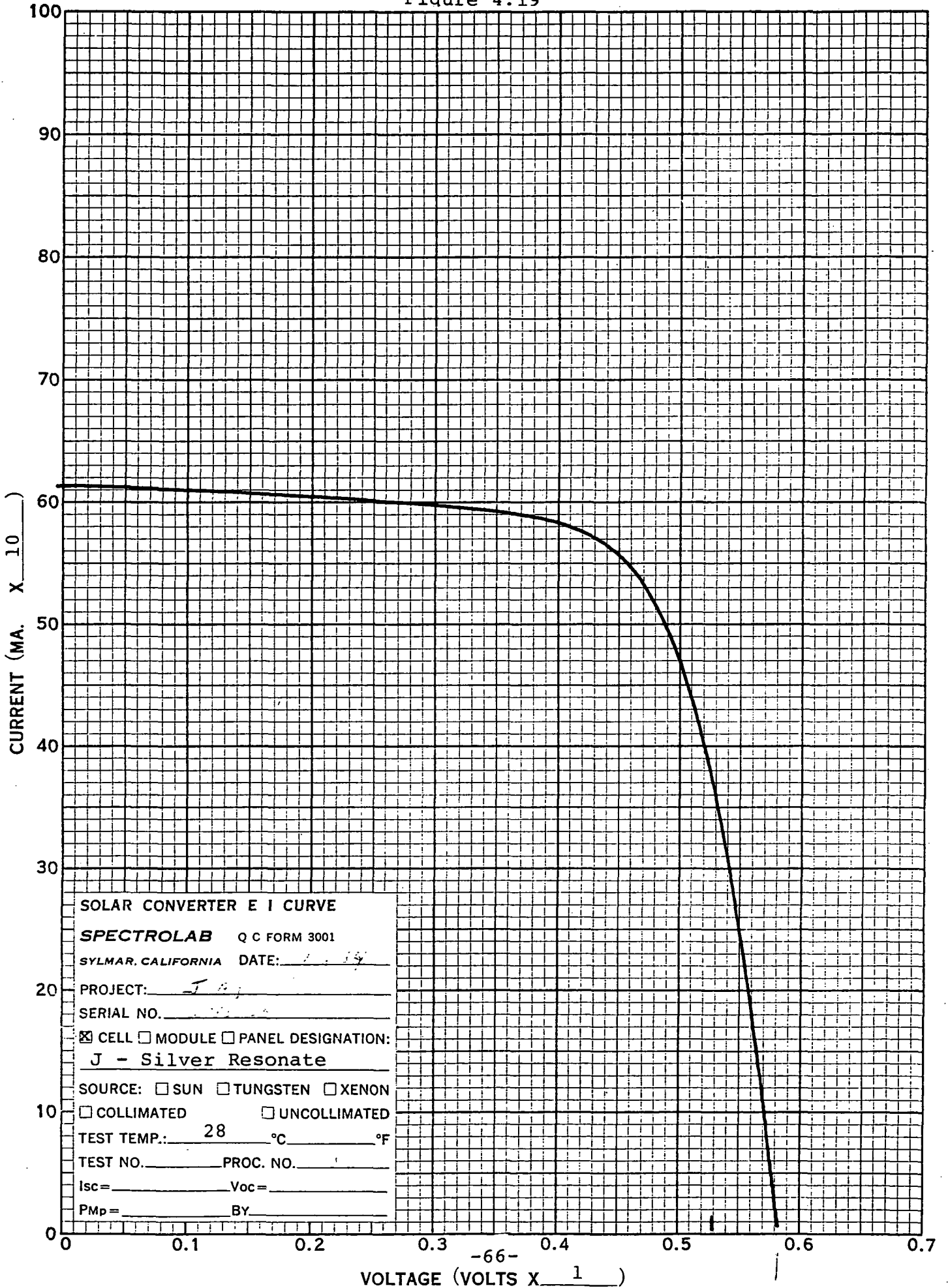


Figure 4.20

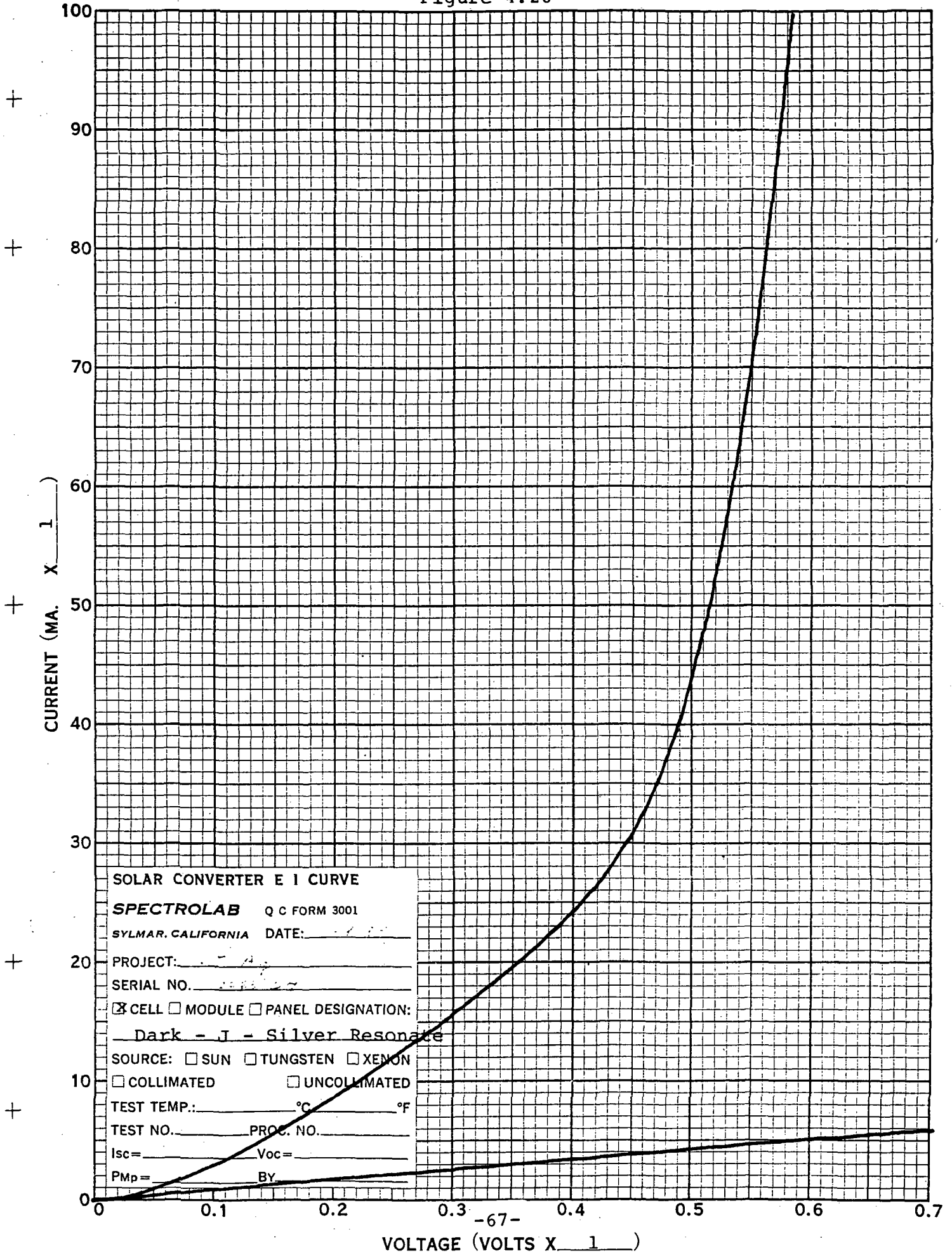
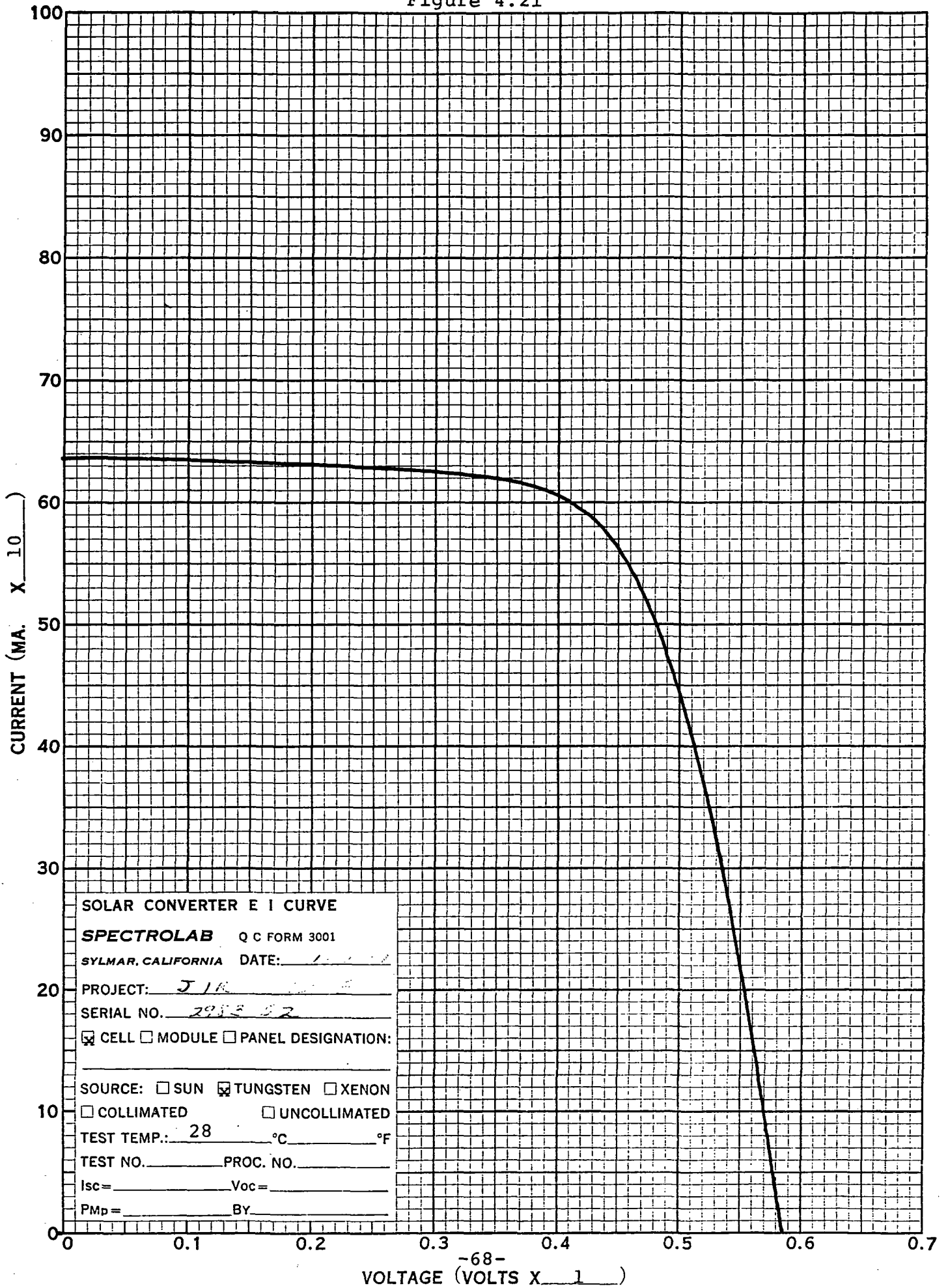


Figure 4.21



SOLAR CONVERTER E I CURVE

SPECTROLAB Q C FORM 3001

SYLMAR, CALIFORNIA DATE: 1/1/77

PROJECT: JIR

SERIAL NO. 2953 52

☒ CELL ☐ MODULE ☐ PANEL DESIGNATION:

SOURCE: ☐ SUN ☒ TUNGSTEN ☐ XENON

☐ COLLIMATED ☐ UNCOLLIMATED

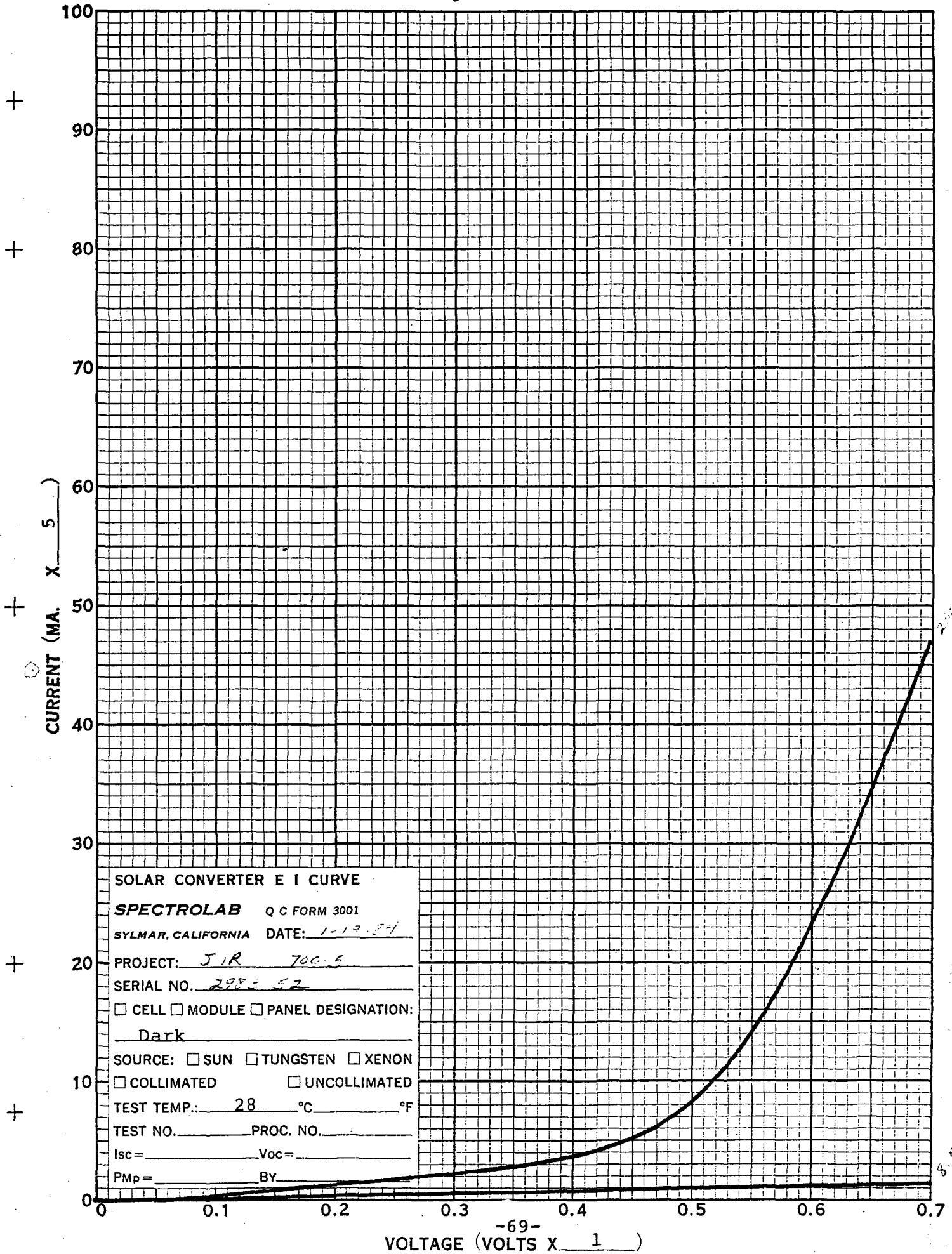
TEST TEMP.: 28 °C °F

TEST NO. PROC. NO.

Isc= Voc=

PMP= BY

Figure 4.22



-69-
VOLTAGE (VOLTS X 1)

Figure 4.23

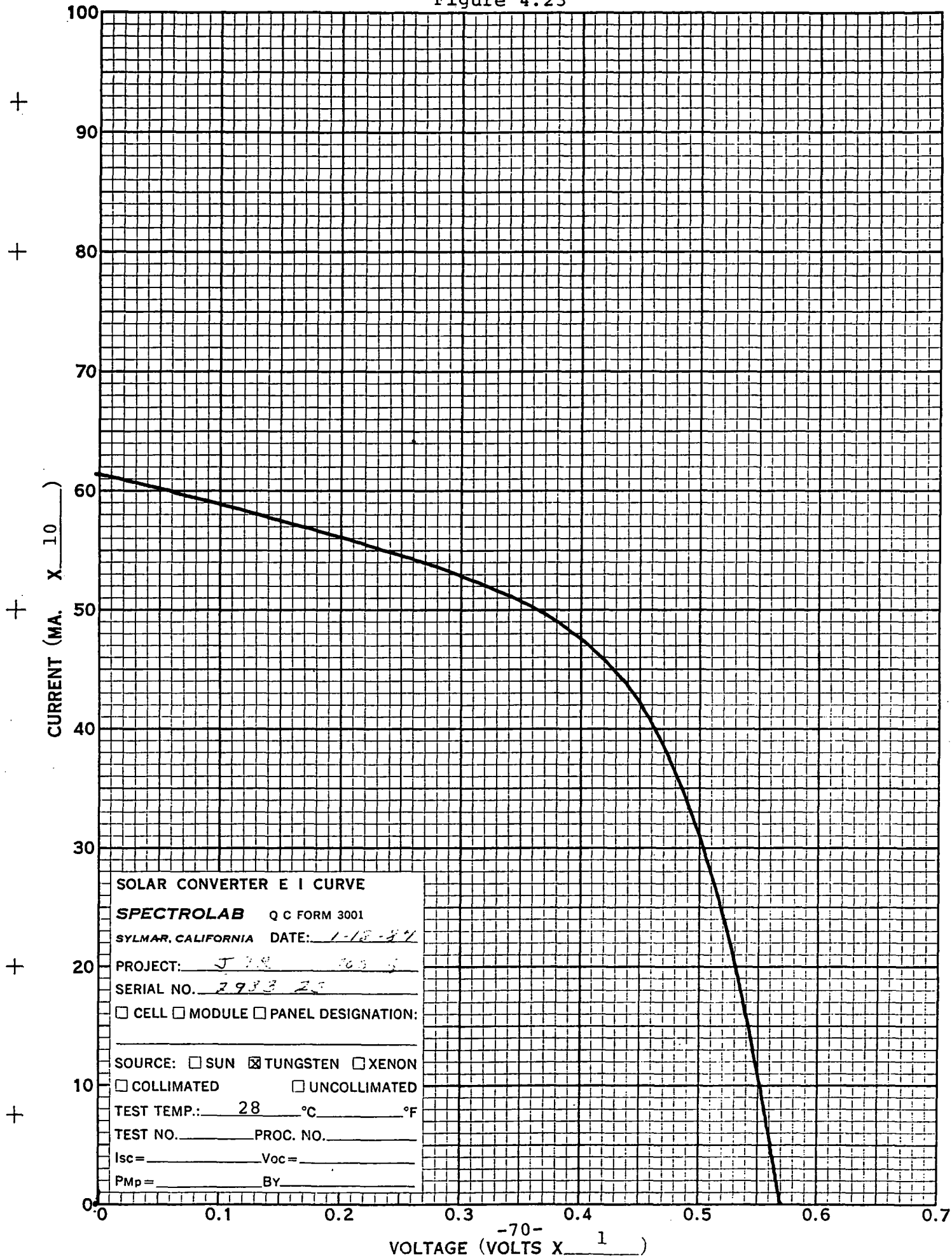


Figure 4.24

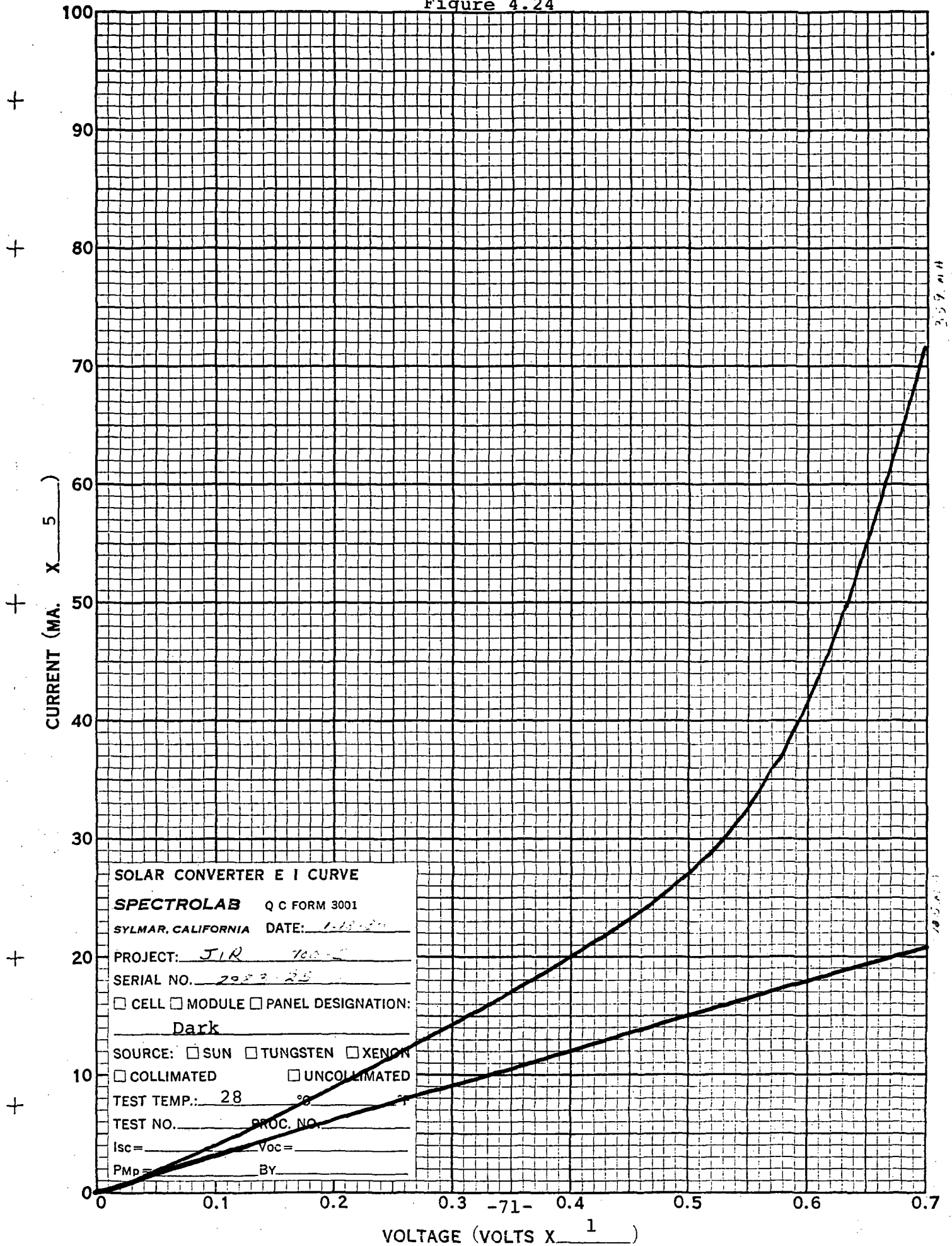


Figure 4.25

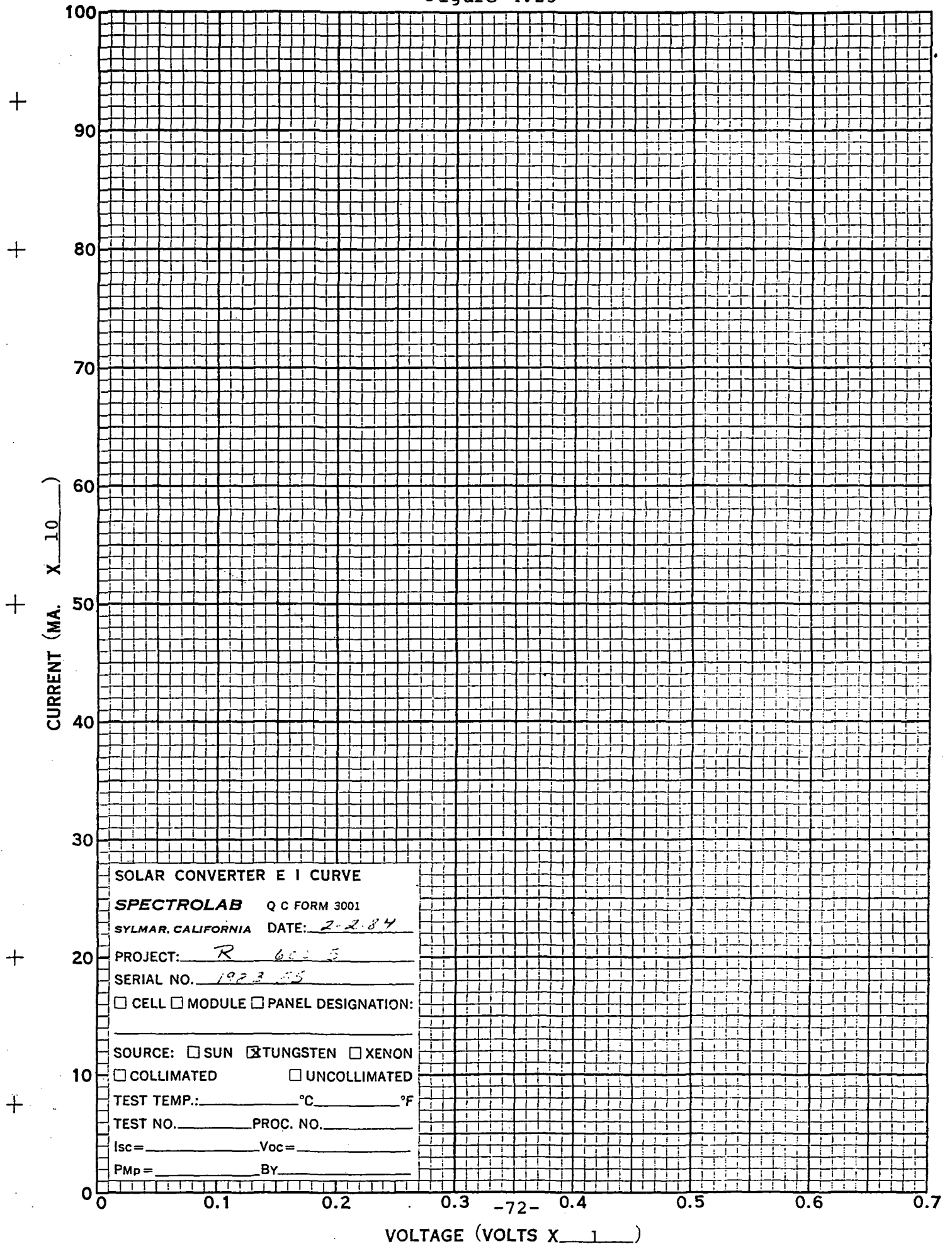


Figure 4.26

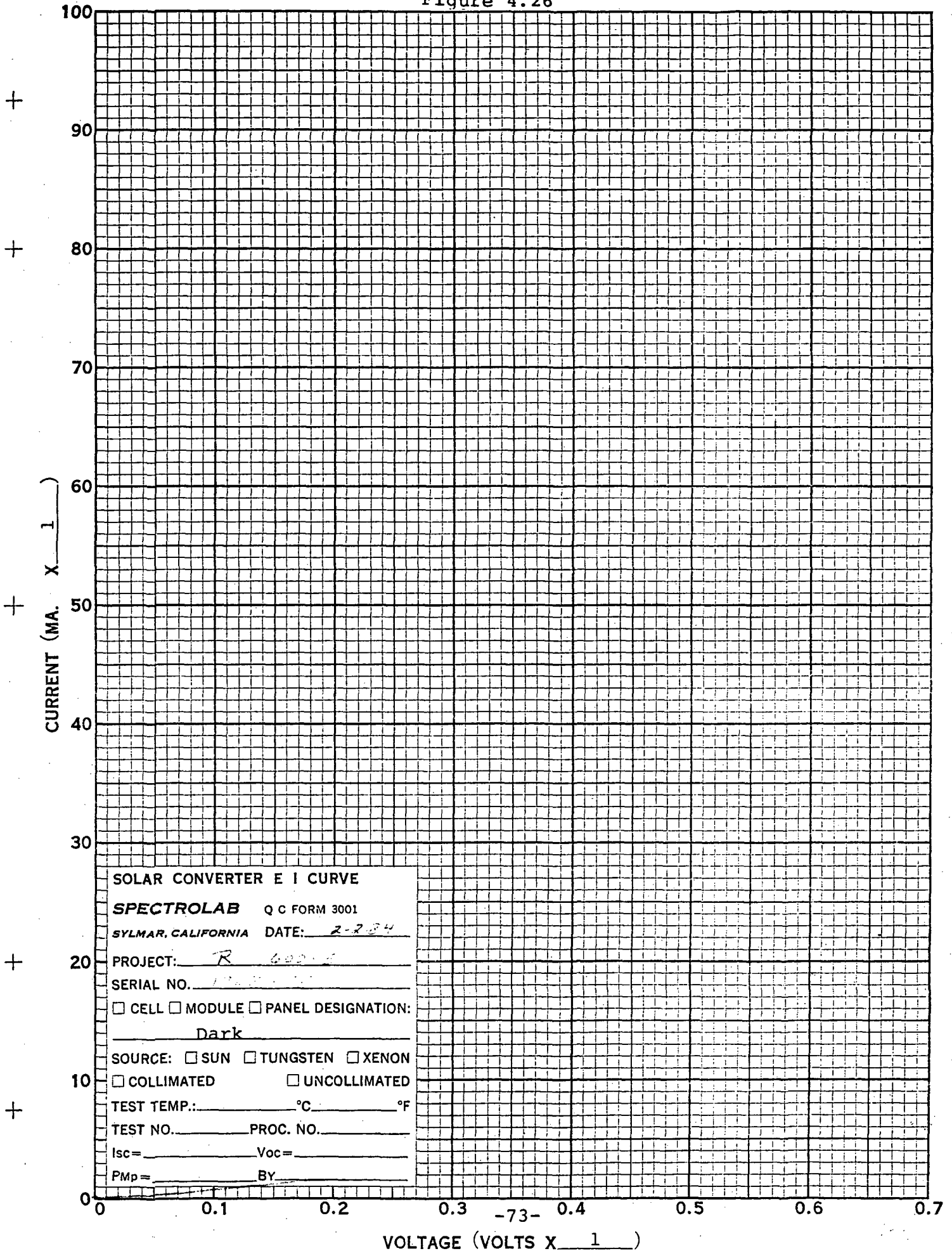


Table 4.7

PRODUCT INFORMATION

Formulation % by Weight

<u>Item</u>	<u>F-86</u>	<u>F-87</u>
Titanium Hydride (TiH_2)	.55	.55
Molybdenum Powder	14.40	14.40
Tin Powder	57.60	57.60
Frit L1571A	4.45	4.45
Silver Flake Type C	8.00	-
Bismuth Powder	-	8.00
Vehicle V-38	15.00	15.00
Identification	S	T

heating on a hot plate to cause the neodecanoate to act as sintering agent. This attempt was also unsuccessful.

Two new pastes were procured from Electrink. Table 4.8 shows the formulations. These formulations were based on experience at Electrink on silver inks. Paste S is similar to paste J with silver flake added, and paste T has bismuth added. The printed cells were sintered at temperatures of up to 650°C but did not show good curve shape. Typical light and dark curves are shown in Figures 4.27 and 4.28. Higher temperatures and longer times produced low shunt resistance. Both S and T behaved in a similar fashion. More experimentation was done on the molybdenum oxide paste (paste M). Sintering temperatures up to 825°C under H₂ were used. The best cell IV curves are shown in Figures 4.29 and 4.30. Cells fired at higher temperatures showed severe shunts. The low short circuit current is difficult to explain and may be due to an opaquing layer forming on the cell surface. Cells fired at temperatures of 825 and 850°C showed metallic-like grid patterns which were solderable. However, none of the solderable cells had measurable IV curves. Spectrolab has been unable to reproduce earlier research done on this paste system.

Table 4.8

PRODUCT INFORMATION

Formulation % by Weight

<u>Item</u>	<u>F-86</u>	<u>F-87</u>
Titanium Hydride (TiH_2)	.55	.55
Molybdenum Powder	14.40	14.40
Tin Powder	57.60	57.60
Frit L1571A	4.45	4.45
Silver Flake Type C	8.00	-
Bismuth Powder	-	8.00
Vehicle V-38	15.00	15.00
Identification	S	T

Vehicle Formulation

<u>Item</u>	<u>V-38</u>
α -terpineol	43.62
Butyl Carbitol Acetate	43.62
Ethyl Cellulose N-14	9.76
Thixatrol ST	3.00

Table 4.8 (continued)

Frit Composition - % by Weight

<u>Item</u>	<u>Frit L1571A</u>
PbO	60
B ₂ O ₃	30
SiO ₂	10

Materials Sources

<u>Material</u>	<u>Designation</u>	<u>Source</u>
Titanium Hydride (TiH ₂)	77113	Alfa-Ventron, Danvers, MA
Silver Flake	C	Metz Meta-lurgical, Plainfield, Nj
Molybenum Powder	280/325	GTE Sylvania, Towanda, PA
Tin Power 325 Mesh	00352	Alfa-Ventron, Danvers, MA
Frit No. L1571A	L1571A	Americal Porcelain Enamel Co. Muskegan, Mich.
α-terpineol	TX 75	MCB Chem. Cincinnati, OH
Butyl Carbitol Acetate	BX 1722	MCB Chem. Cincinnati, OH
Ethyl Cellulose	N-14	Hercules, Wilmington, DE
Thixatrol (thickner)	ST	NL Industries, Hightstown, NJ
Elvacite (acrylic resin)	2042	Dupont, Wilmington, DE
Bismuth Powder	00046	Alfa-Ventron, Danvers, MA

Figure 4.27

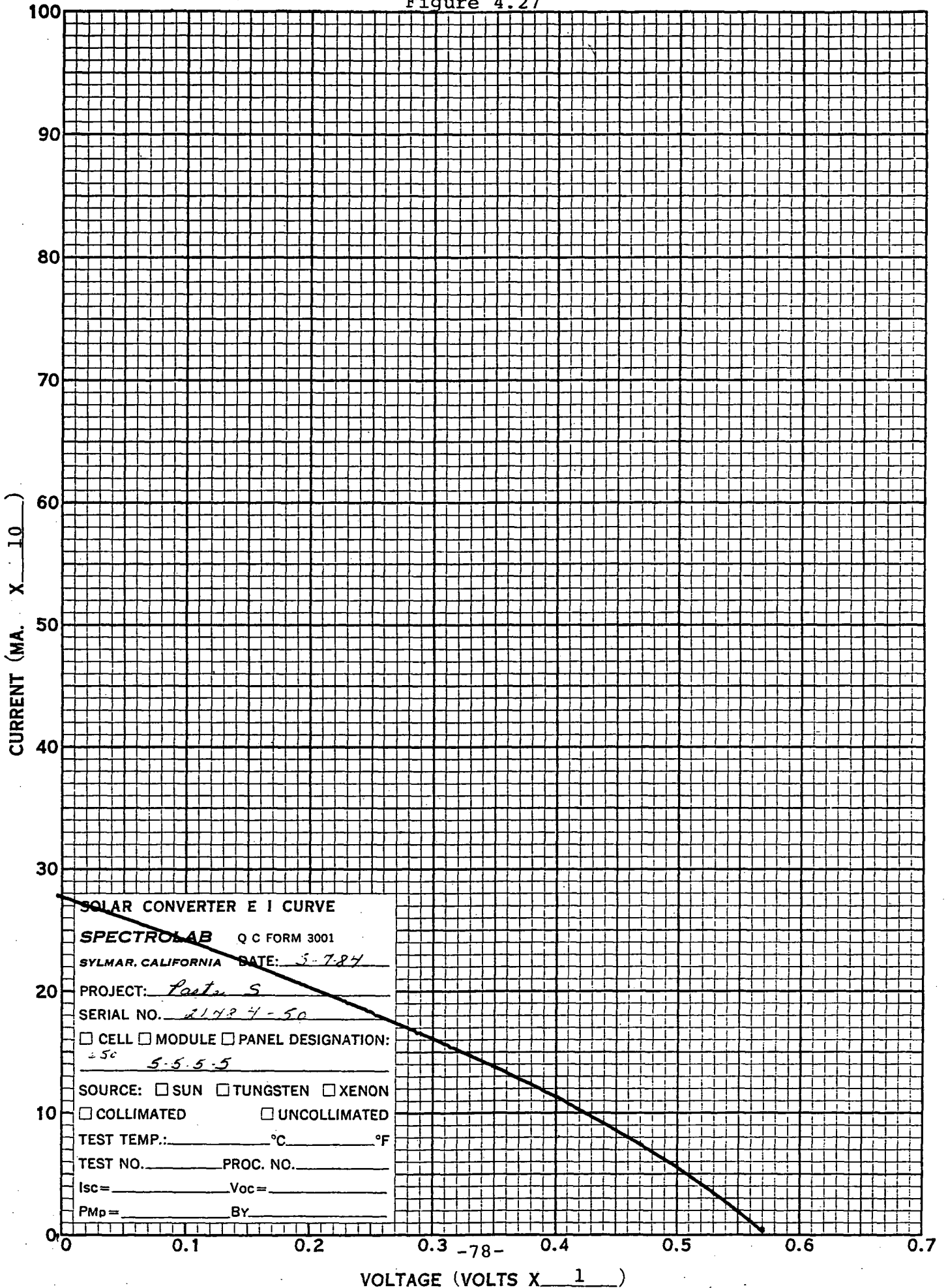


Figure 4.28

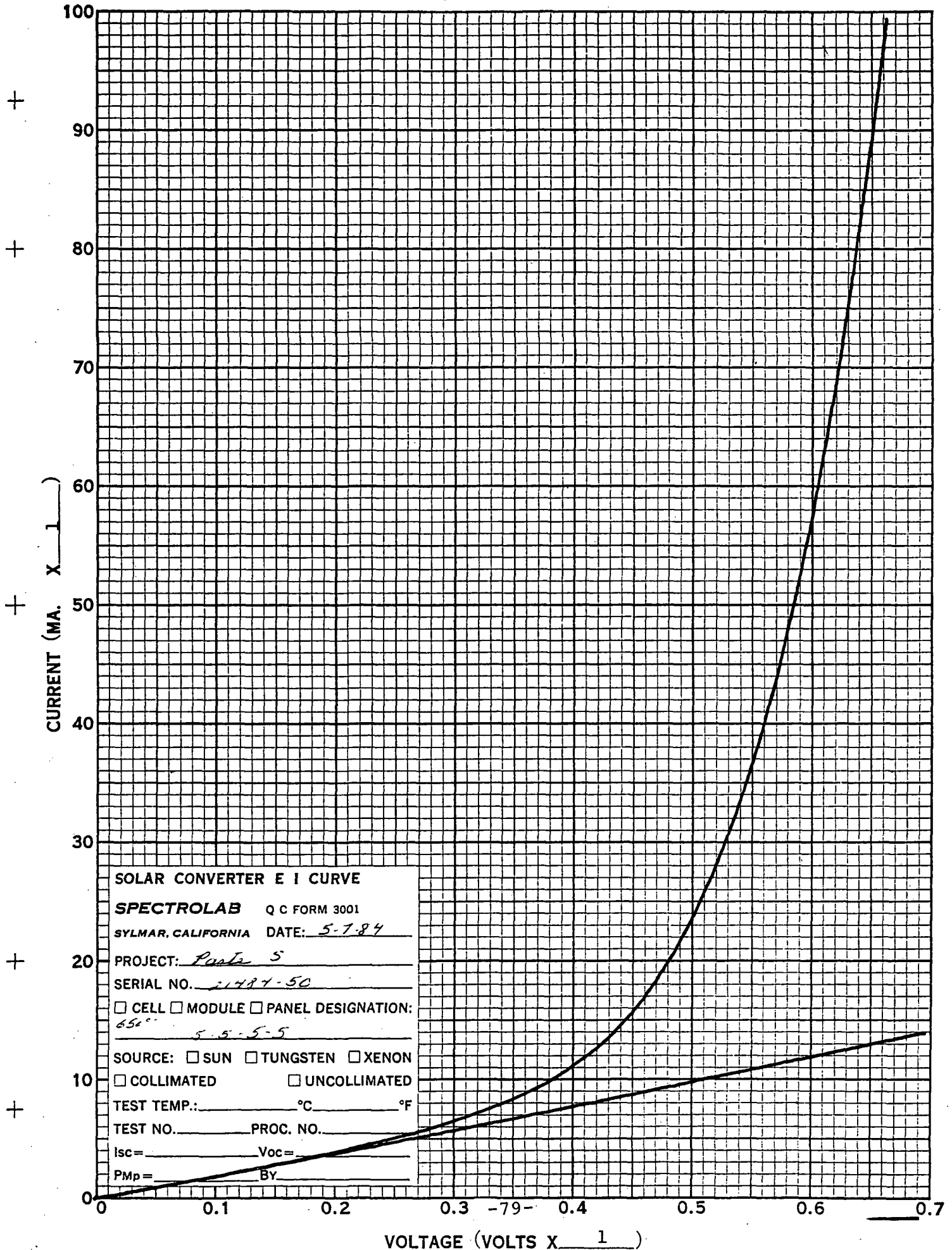


Figure 4.29

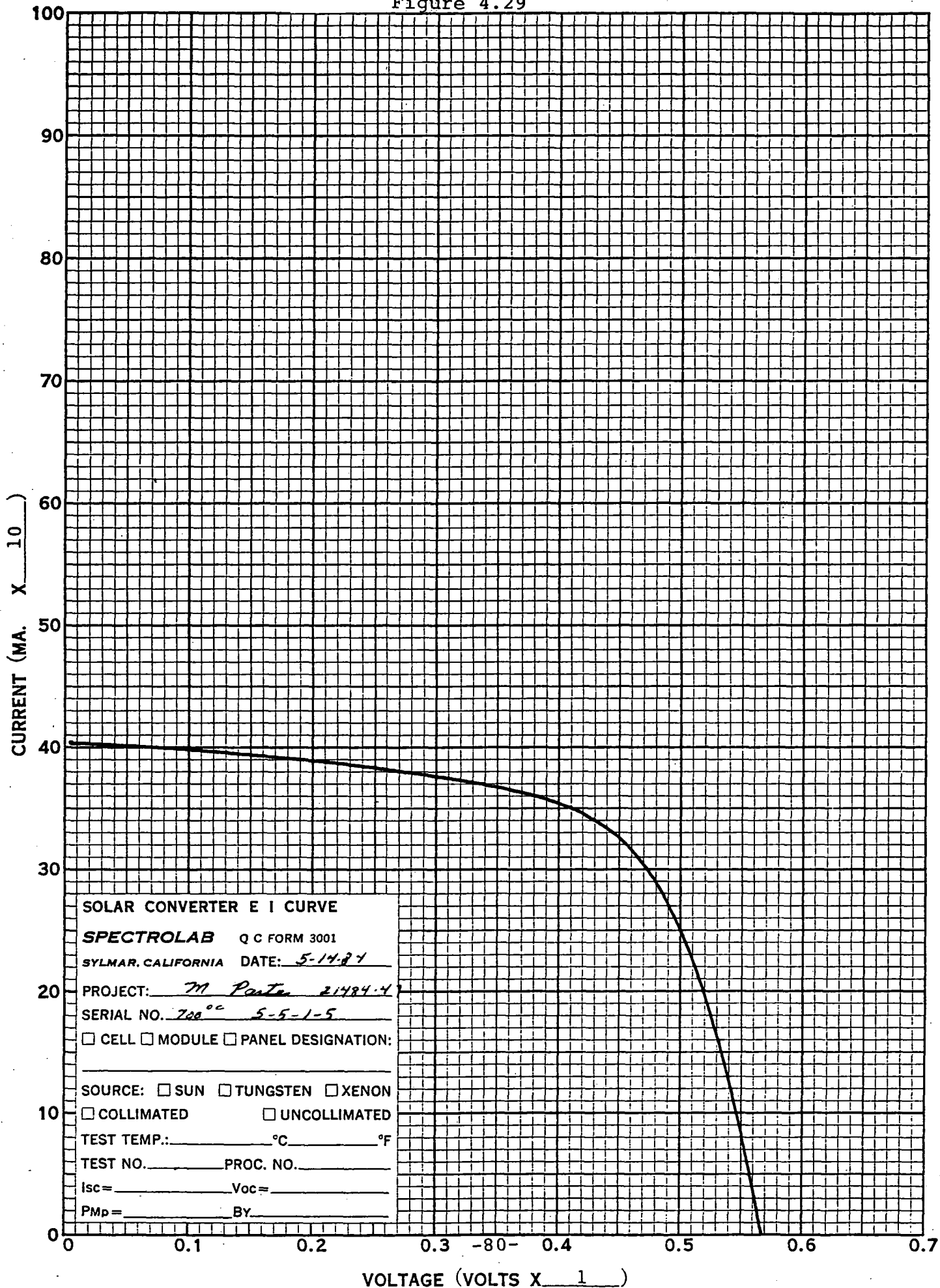
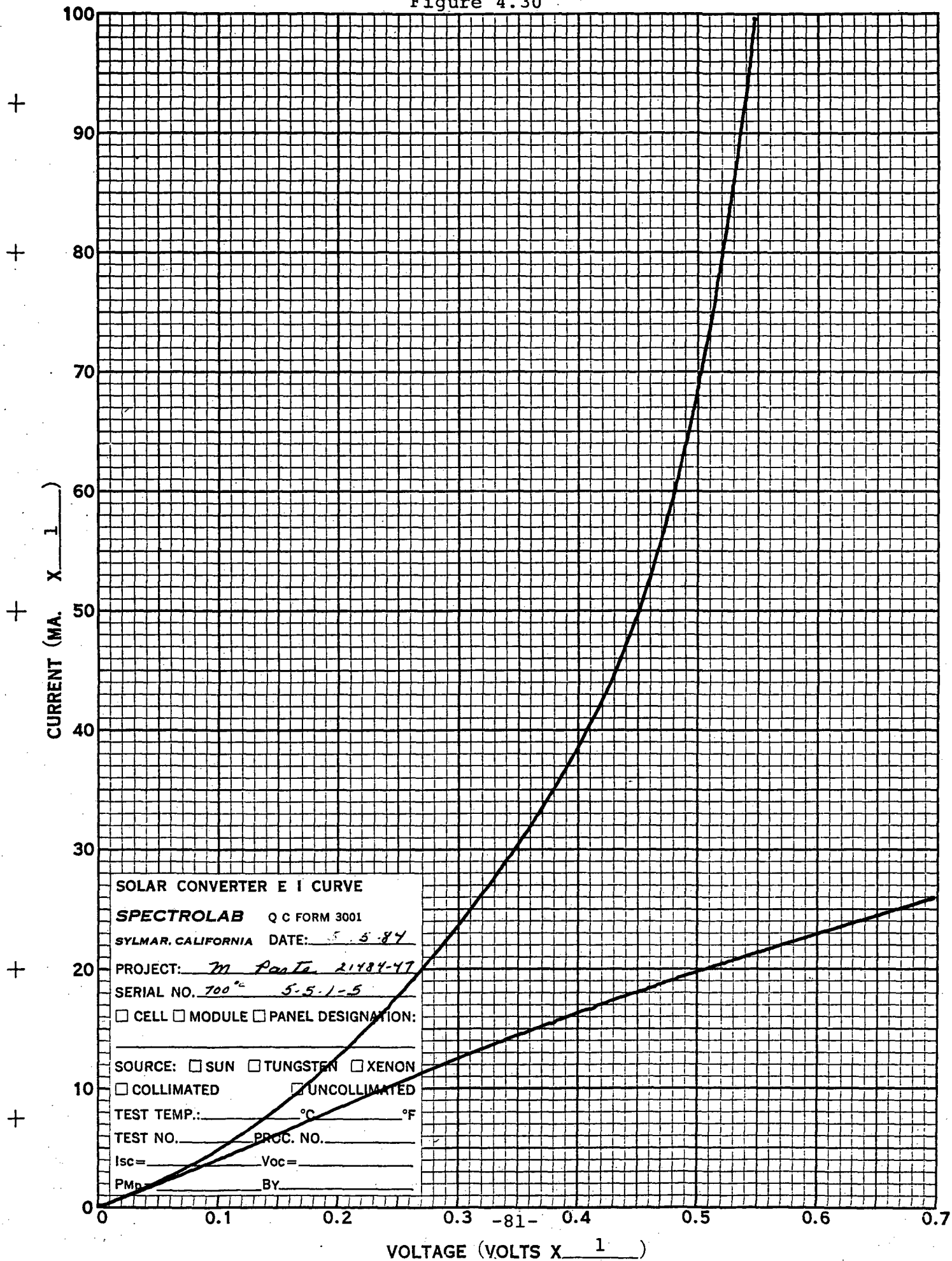


Figure 4.30



Section 5.0

TWO-STEP PROCESS

In view of the difficulties in soldering to the Mo/Sn pastes, several experiments were conducted using a two step screen-printing procedure. One step would put down a small silver paste soldering pad and the other the Mo/Sn grid pattern.

The first experiment was done using paste F503. The cells were printed with the front metallization pattern missing the ohmic pad. The 600°C prefire at 18"/min. was then performed. Silver paste was printed on the ohmic pads overlapping the Mo/Sn paste. The cells were fired at 600°C in the IR furnace at 48"/min. with an 18" zone at 400°C and a 24" zone at 750°C. The cells were next fired in H₂ for 5 min. at 600°C. The best cell had the following characteristics when tested by contacting the Mo/Sn metallization: $V_{OC} = 586$ mV, $I_{SC} = 650$ mA, $I_{500} = 448$ mA. When the cell was contacted on the Ag pad the ISC fell to 080 mA. There was no ohmic contact between the two metallization types. Cells were also processed with 500 and 400°C prefire temperatures, but had similar characteristics. Interconnects were successfully soldered to the ohmic pad. Cells were first printed with J and E pastes, and prefired at 600°C. The pattern left the soldering pad bare. Silver paste was then printed over the solder pad area overlapping onto the Mo/Sn metallization. The cell was then fired in air at 750°C (48"/min., 24" zone at 400°C and 18" zone at 750°C). The cells were sintered in H₂ for 5-30 min. at 600-650°C. The

best cell is shown in Figures 5.1 and 5.2. There is good continuity between the ohmic pad and the rest of the metallization, but series resistance is too high.

Figure 5.1

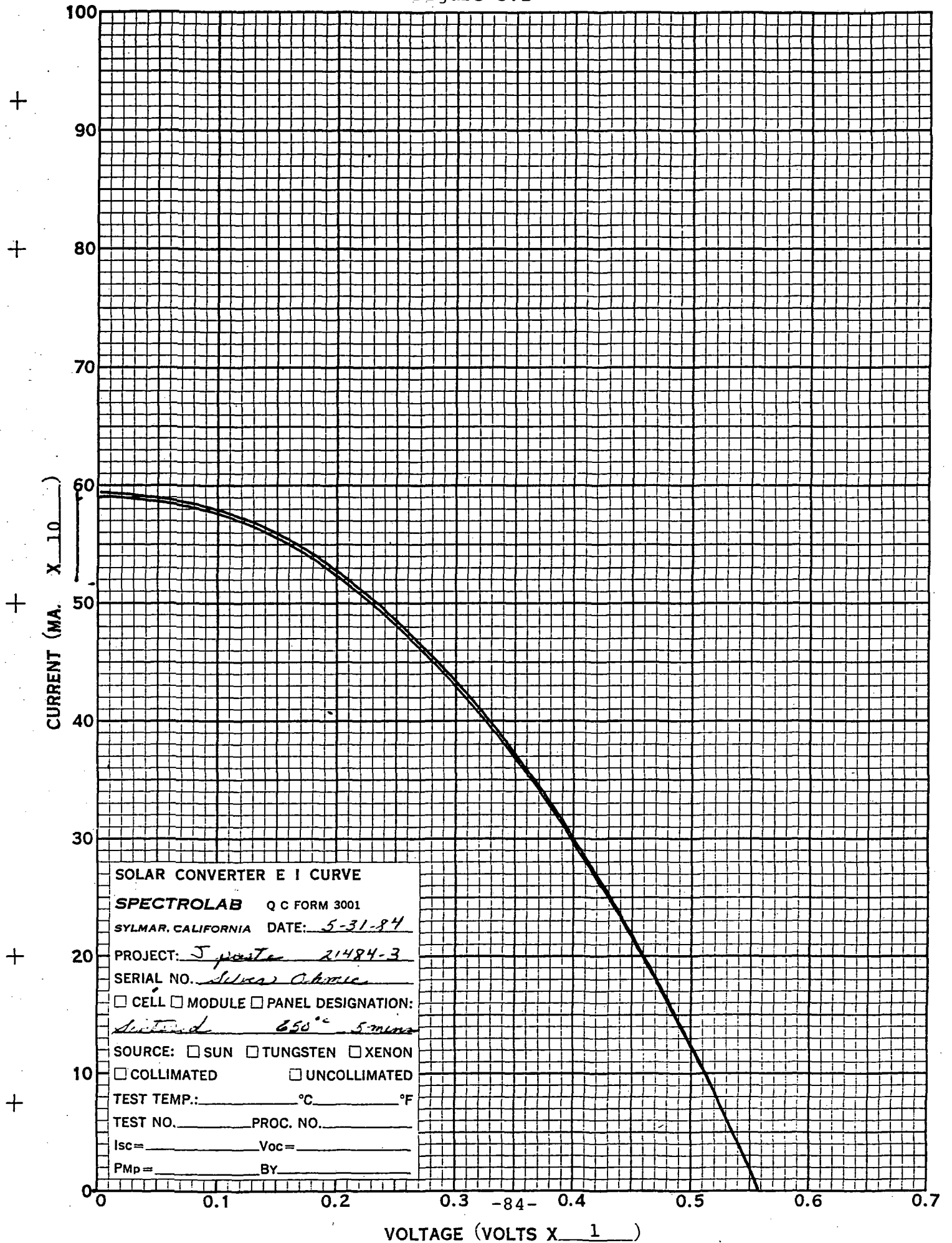
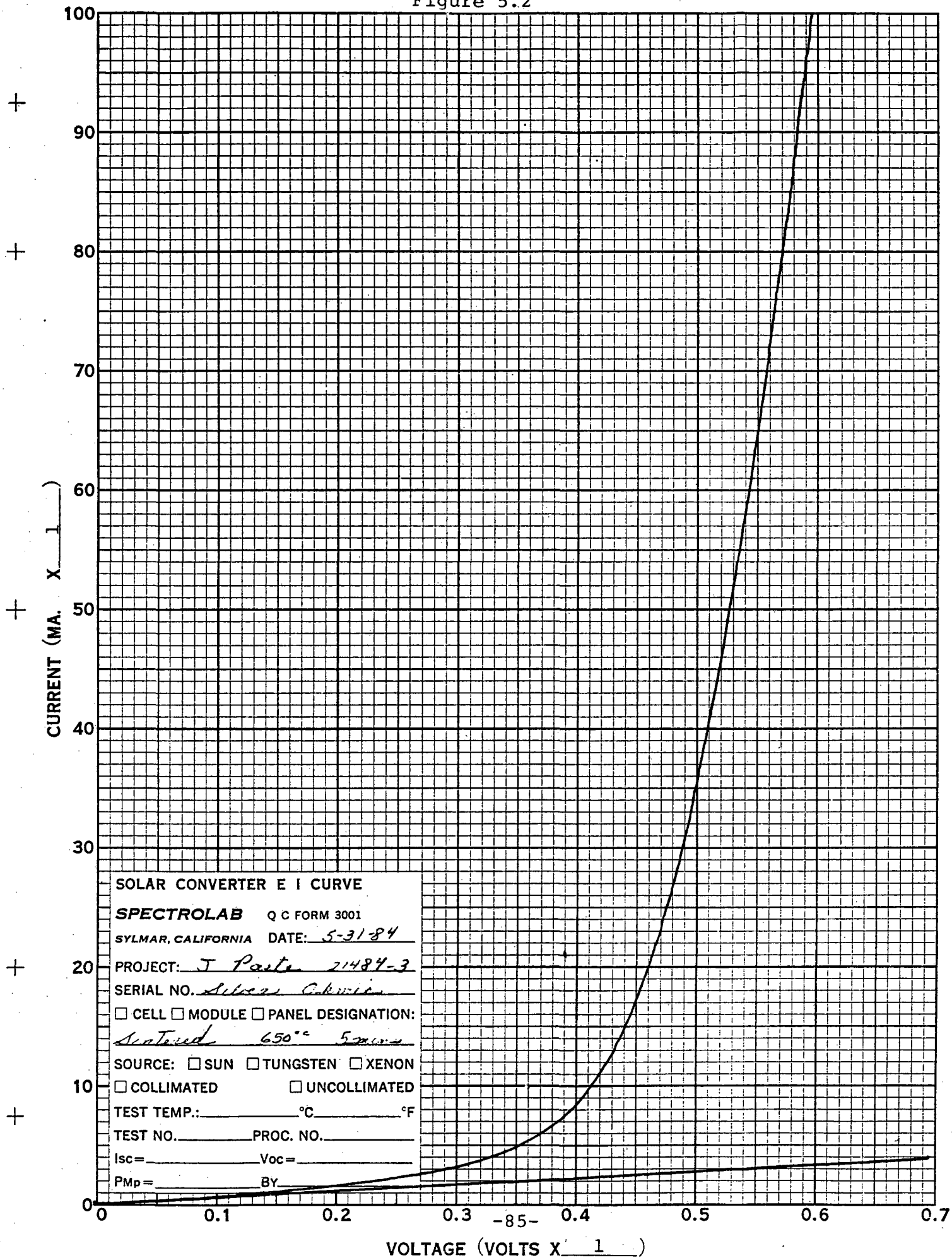


Figure 5.2



Section 6.0

HOT STAGE SEM

A visit was made to Microscopy Research Laboratories, Inc. in Sommerville, NJ. This company has a controlled atmosphere SEM with a heated sample stage. Figure 6.1 shows a schematic of the instrument. The sample is placed in a sample holder and can be exposed to any atmosphere up to 5 torr while being heated and observed via the SEM. Video tapes of the SEM image are made as the sample is being heated. A sample of the dried J paste was observed with the instrument. Initially when O₂ was introduced and the sample heated to 500°C, tin particles melted to globules at 230°C but did not wet surrounding particles. The sample was returned to room temperature and H₂ introduced to the sample. The sample was heated slowly to 800°C. The sample showed minor changes until a temperature of 700°C was reached, when a rapid wetting and movement of the particles was seen. A well sintered continuous structure was formed. Figures 6.2 and 6.3 show SEM photographs before and after this redistribution.

The use of x-ray analysis concurrently with this technique can also prove valuable. Figure 6-4 and 6-5 are micrographs of Paste J modified with indium resonant that have been printed and dried. Figures 6-6, 6-7, and 6-8 are energy dispersive x-ray analyses for silicon, tin and molybdenum respectively; these pictures should be matched to Figure 6-5. A higher density of dots indicates more of the element is present. Indium was not

CONTROLLED ATMOSPHERE SCANNING ELECTRON MICROSCOPY

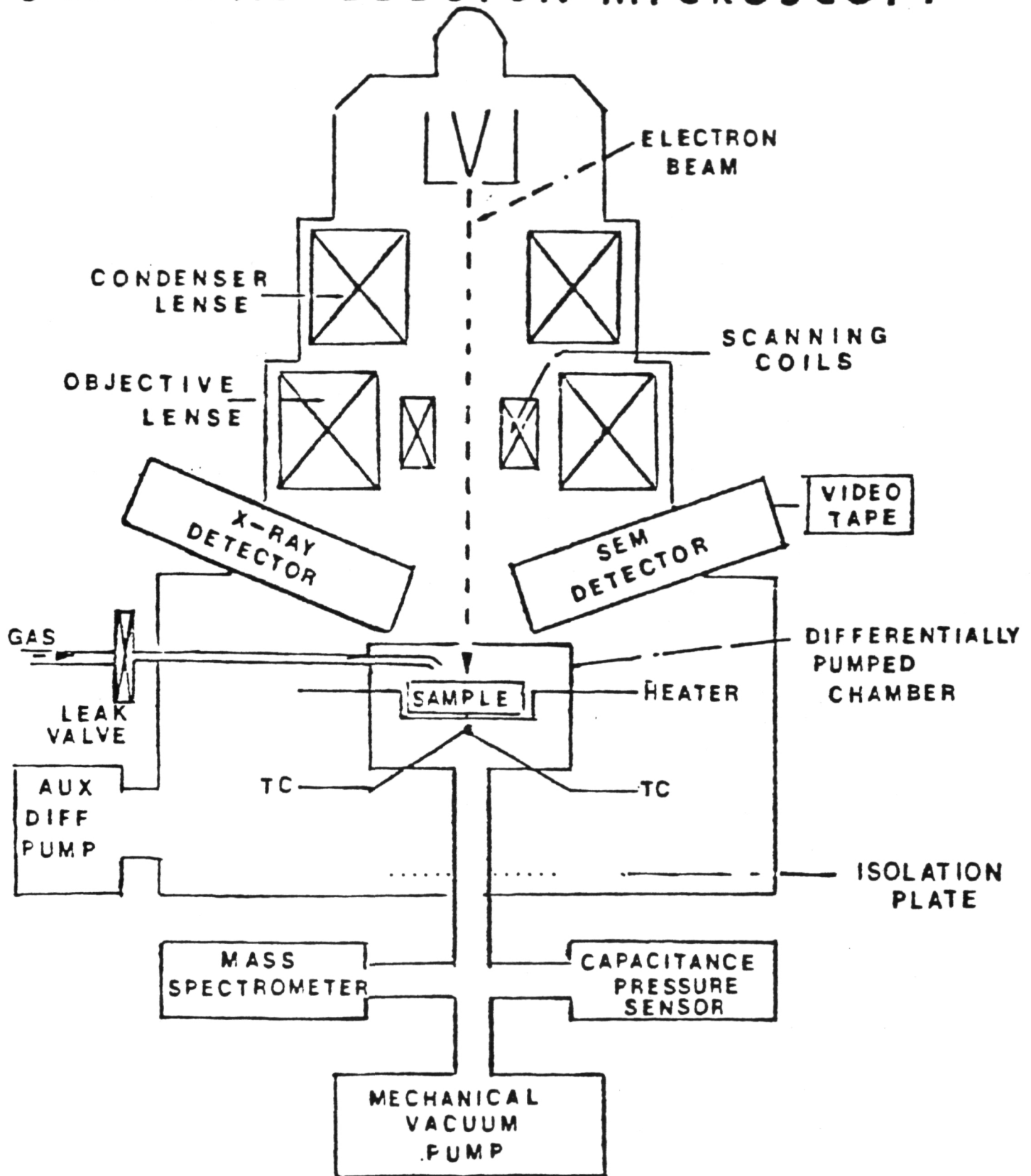


Figure 6.1
MICROSCOPY RESEARCH LABORATORIES, INC.

Figure 6.2
PASTE J, 3000X, PRIOR TO HEATING

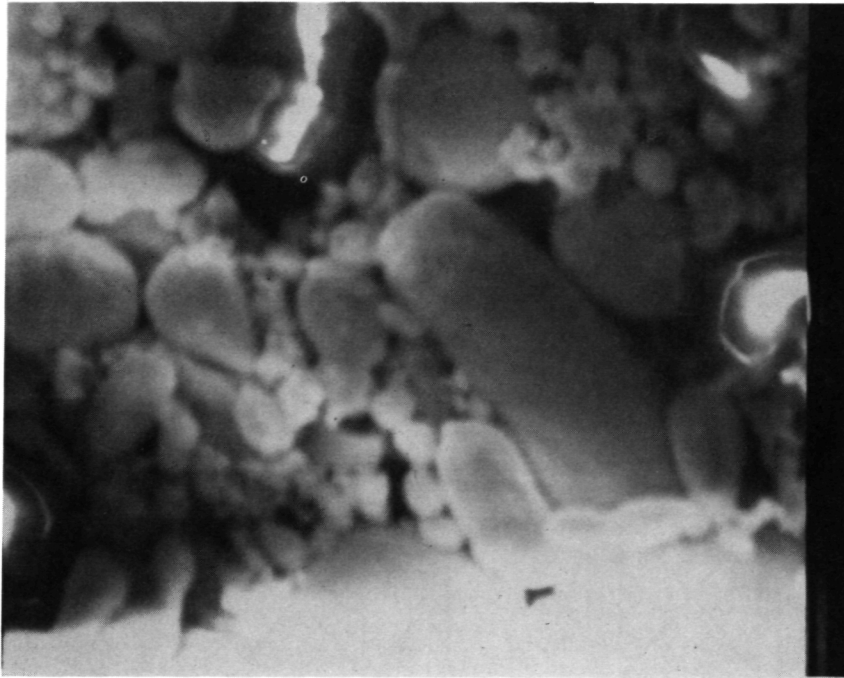
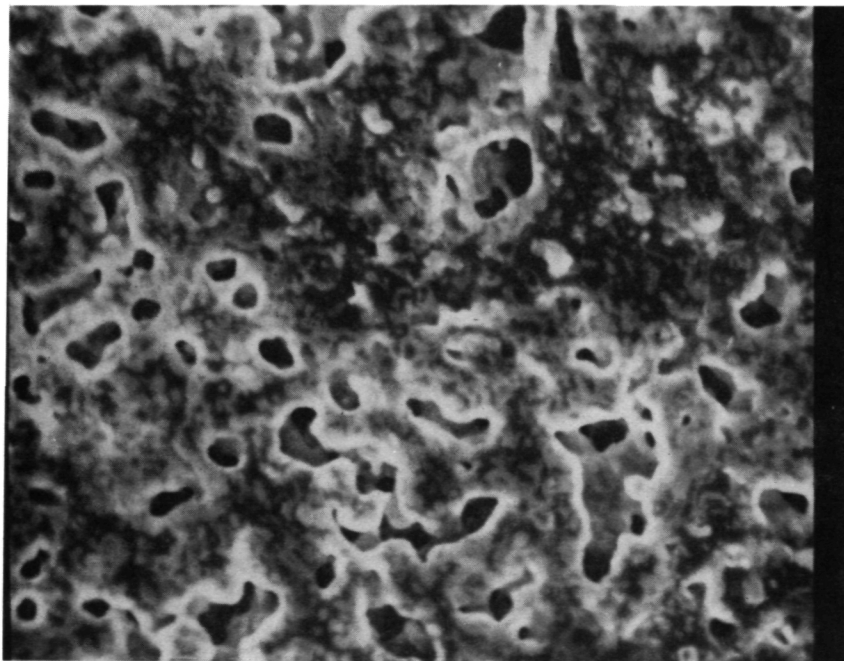


Figure 6.3
PASTE J, 3000X, AFTER HEATING



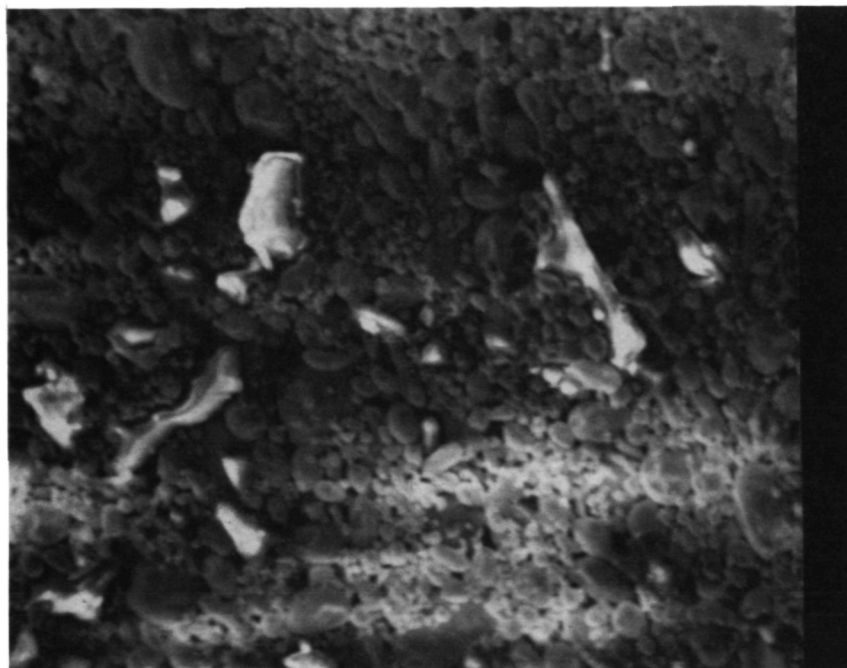


Figure 6.4
MODIFIED PASTE J 500X

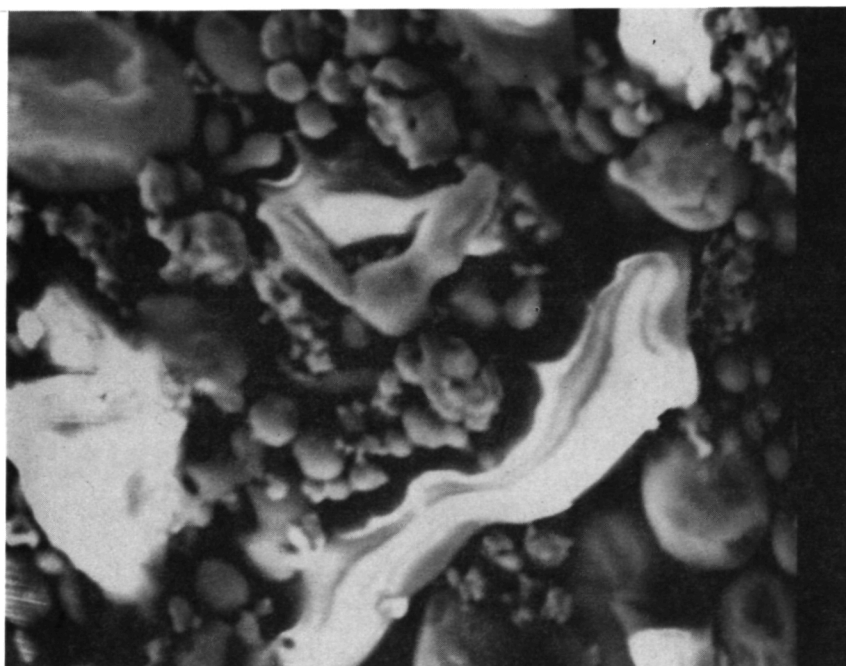


Figure 6.5
MODIFIED PASTE J 1500X

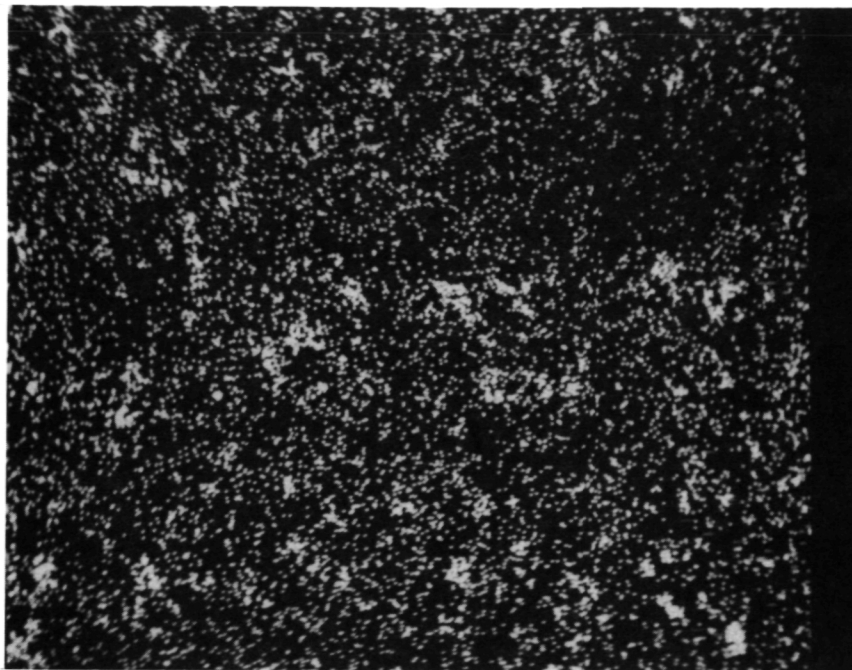


Figure 6.6
SILICON MAP OF 6-5

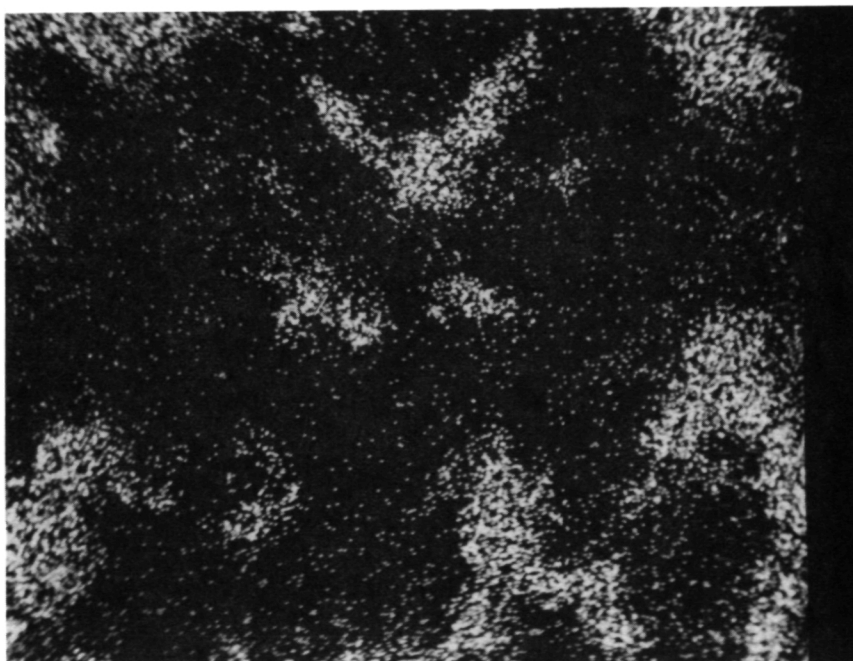


Figure 6.7
TIN MAP OF 6-5

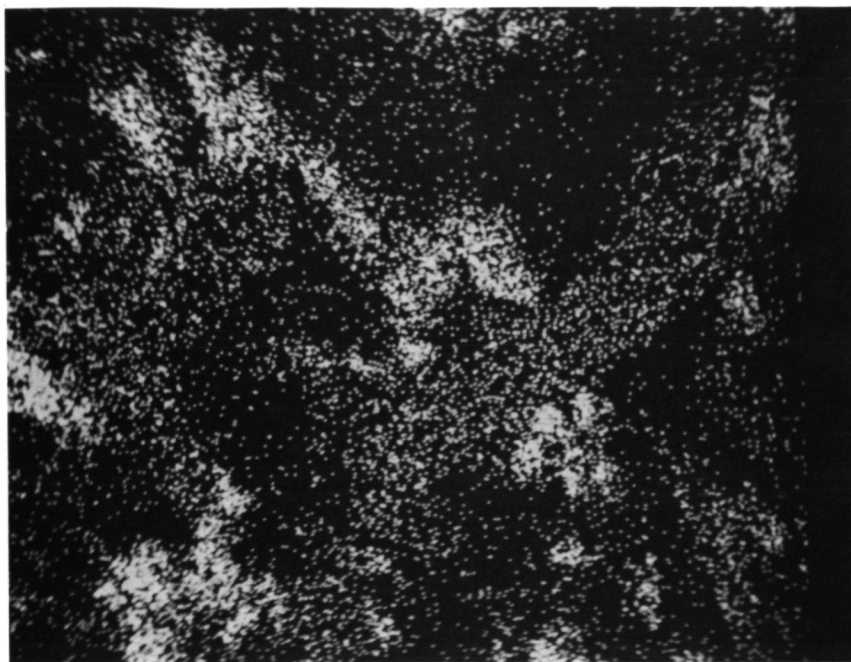


Figure 6.8
MOLYBDENUM MAP OF 6-5

present in high enough concentration to be detected. This technique enables the identification of the composition of particular particle which can then be observed during heating. This sample showed similar behavior to the first with formation of molten tin globules that did not wet the surrounding particle until higher temperatures were reached. Figure 6-9 and 6-10 show the paste after heating. Elemental analyses for Pb, Sn, and Mo referenced to 6-10 are shown in Figures 6-11, 6-12, and 6-13. Complete wetting of the tin globules has not occurred. The tin globules that are created appear to have some sort of a surface coating which inhibits wetting. We were unable to find a way to break that coating and cause wetting at temperature low enough for cell processing.

One set of experiments was done using the L paste and sintering for long periods of time at lower temperatures without drying. It was hoped that the nonwetting of the molten tin particles was caused by an oxide which would be broken down in time by reaction with hydrogen. Cells were printed, dried and placed in the sintering furnace under H_2 at $400^\circ C$. After four hours in the furnace cells did not show signs of sintering.

This technique was of great value in elucidating possible mechanisms that cause problems with these pastes. It was unfortunate that the resource was discovered late in the contract and not fully utilized. We feel this type of analysis will be of great value in research in thickfilm pastes.

The true power of this analytical technique can best be seen when the video tapes of a run are viewed. Video tapes are available for interested readers.

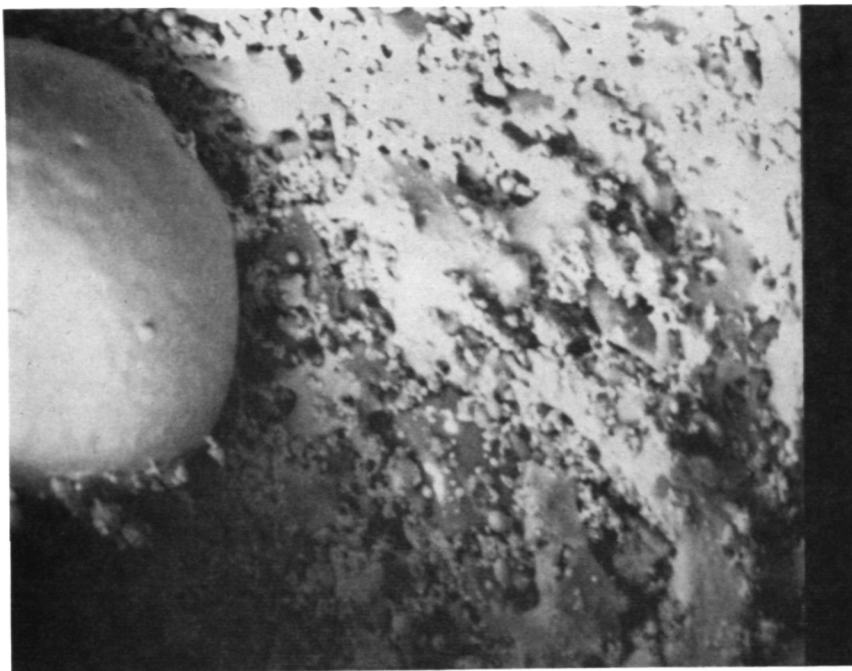


Figure 6.9
MODIFIED PASTE JA AFTER HEATING 500X

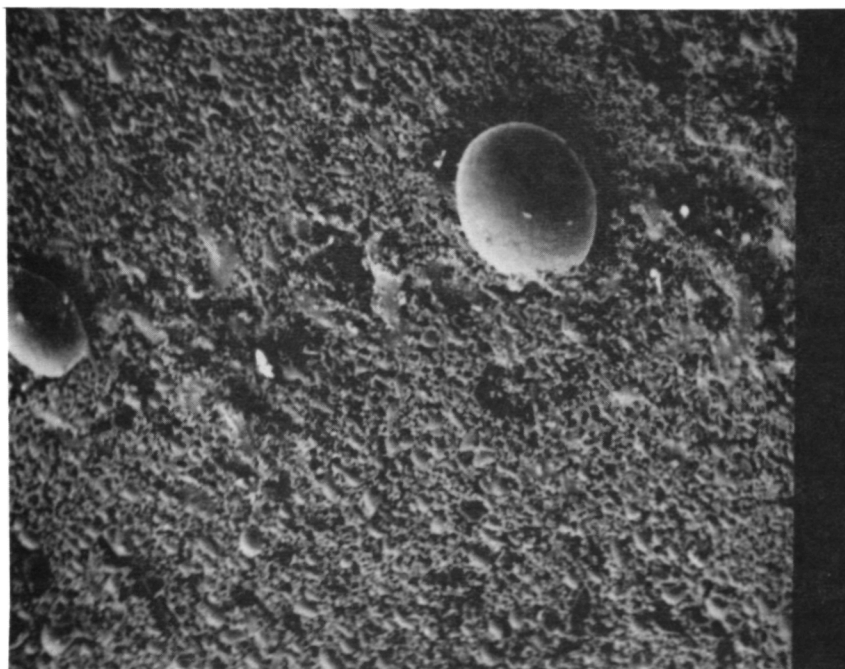


Figure 6.10
MODIFIED PASTE J AFTER HEATING 150X

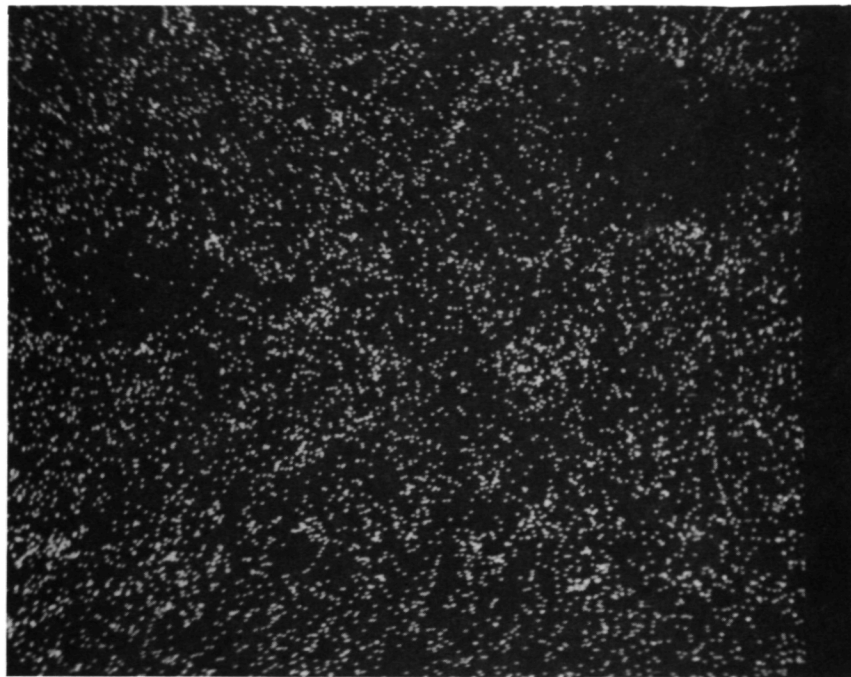


Figure 6.11
LEAD MAP OF 6-10

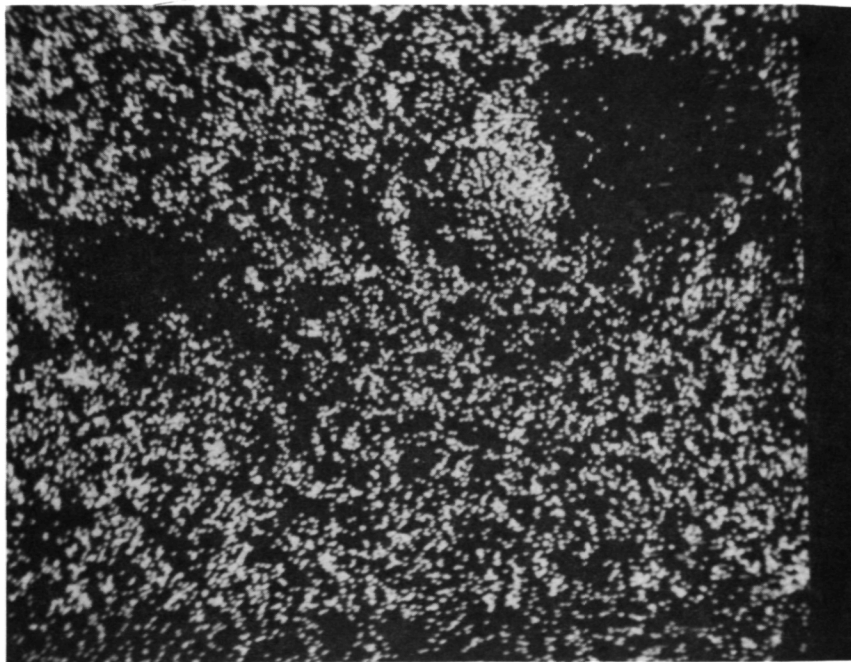


Figure 6.12
TIN MAP OF 6-10

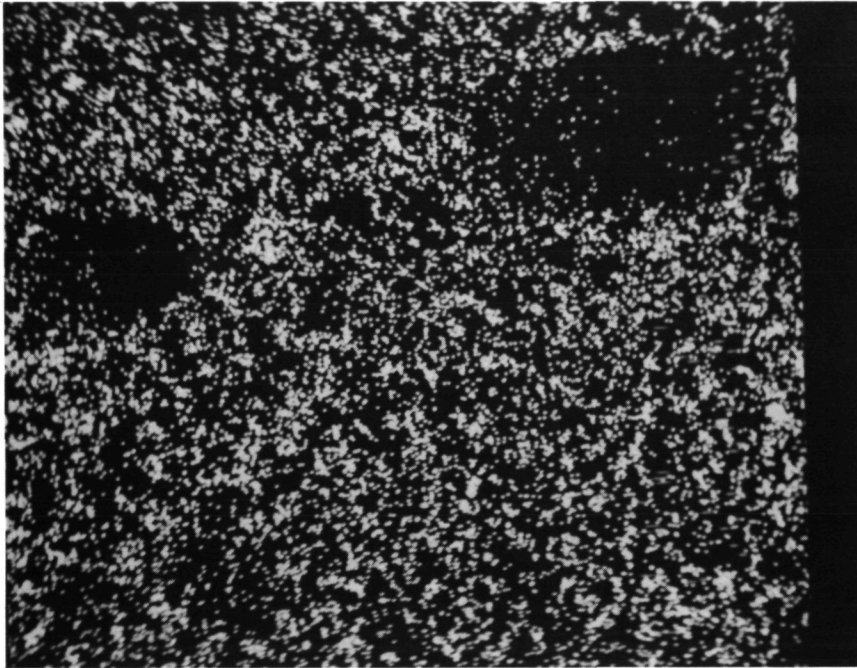


Figure 6.13
MOLYBDENUM MAP OF 6-10

Section 7.0

CONCLUSIONS AND RECOMMENDATIONS

No satisfactory cells were made using any of the molybdenum/tin pastes used as a complete replacement for conventional silver pastes. The major problem is the inability to form a bond between the pastes and silicon that withstands soldering. This problem can be overcome using a two step process where any interconnection to the cell is done at small pads of conventional screen printed silver. Spectrolab feels that the most promising use of the molybdenum/tin metallization system would be this two step process with a silver paste serving as the soldering pad. The Mo/Sn system would compete with silver economically if silver prices rose and could serve as a backup process.

Toward the end of this contract the use of a heated stage SEM with reactive gases was a great help in elucidating problems and suggesting solutions. Spectrolab feels this tool should be further investigated and used in thick film paste research.